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Municipal Waste Combustion Study
Sampling and Analysis of Municipal Waste Combustors

Little (Arthur D.), Inc., Cambridge, MA

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The purpose of this document is to provide guidance on sampling and analysis methods to assist federal, state, and local environmental authorities in reviewing plans for operations and testing of MSW combustors. The sampling and analysis procedures outlined here are intended to represent state-of-the-art methods that may be useful in determining the regulatory compliance status of MSW incineration facilities and in assessing their environmental impacts. These same methods may be useful in reseach and development programs related to MSW combustion technology, standard setting, etc.

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Municipal Waste Combustion Study

Sampling and Analysis of Municipal Waste Combustors

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FOREWORD

This document is intended to serve as a resource document outlining recommended sampling, analysis and monitoring procedures for municipal solid waste combustion facilities. The effort reported here has focused on gathering information on probable measurement requirements and on available methods that may meet those requirements. Critical evaluations of alternative methods and recommendations to fill gaps in available methodology were outside of the scope of this assignment.

The Arthur D. Little, Inc. effort is part of a major program to develop an EPA report to Congress on Municipal Waste Combustion. The overall effort is being directed by Radian Corporation (G. Wilkins, Project Manager). The Arthur D. Little contribution is being performed under EPA subcontract with Dynamic Corporation (C. Matkovich, work assignment director). L. D. Johnson is the EPA work assignment director for the Arthur D. Little effort. Key Arthur D. Little staff involved in this work are J. C. Harris (to whom comments should be addressed), D. L. Cerundolo, and K. E. Thrun. The Arthur D. Little reference numbers for this work are 55464 and 55465.

I. INTRODUCTION

A. OVERVIEW

This report is an assessment of sampling and analysis methods for municipal waste combustors. The information presented in this report was developed during a comprehensive, integrated study of municipal waste combustion. An overview of the findings of this study may be found in the Report to Congress on Municipal Waste Combustion (EPA/530-SW-87-021A). The Technical volumes issued as part of the Municipal Waste Combustion Study include:

• Municipal Waste Combustion Study: Report to Congress	EPA/530-SW-87-021A
• Municipal Waste Combustion Study: Emissions Data Base for Municipal Waste Combustors	EPA/530-SW-87-021B
• Municipal Waste Combustion Study: Combustion Control of Organic Emissions	EPA/530-SW-87-021C
• Municipal Waste Combustion Study: Flue Gas Cleaning Technology	EPA/530-SW-87-021D
• Municipal Waste Combustion Study: Costs of Flue Gas Cleaning Technologies	EPA/530-SW-87-021E
• Municipal Waste Combustion Study: Sampling and Analysis	EPA/530-Sw-87-021F
• Municipal Waste Combustion Study: Assessment of Health Risks Associated with Exposure to Municipal Waste Combustion Emissions	EPA/530-SW-87-021G

- Municipal Waste Combustion Study: Characterization of the Municipal Waste Combustion Industry EPA/530-SW-87-021H
- Municipal Waste Combustion Study: Recycling of Solid Waste EPA/530-SW-87-021I

B. PURPOSE OF THIS DOCUMENT

The purpose of this document is to provide guidance on sampling and analysis methods to assist federal, state, and local environmental authorities in reviewing plans for operations and testing of MSW combustors. The sampling and analysis procedures outlined here are intended to represent state-of-the-art methods that may be useful in determining the regulatory compliance status of MSW incineration facilities and in assessing their environmental impacts. These same methods may be useful in research and development programs related to MSW combustion technology, standard setting, etc.

C. SCOPE

This document provides an overview of available state-of-the-art methods for sampling and analysis to address testing and monitoring of MSW combustors. For purposes of this report, testing and monitoring are defined as follows:

> "testing" means performing periodic sampling and analysis by EPA-approved or recommended methods to: confirm compliance with any limits that have been imposed by regulatory agencies as permit conditions; generate data that may be used as inputs to environmental risk assessments; and/or support research and development in municipal waste combustion.
>
> "monitoring" means obtaining continuous instrumental measurements of key process parameters and selected pollutants in the emissions to verify that the facility continues to operate "in control".

The testing can be expected to focus on several categories of potential pollutants:

Criteria pollutants: particulates, CO, SO_2, NO_x,

Acid gases: HCl, HF

Trace metals: Cr(III), Cr(VI), Cd, As, Hg, Pb, Be, etc.

Organic pollutants: chlorinated dibenzo-p-dioxins, chlorinated dibenzofurans, and other trace level species that may be indicators of potential environmental impacts

The parameters for which continuous monitoring may be required during routine operation or requested as part of special purpose programs include:

temperature
opacity
carbon monoxide
carbon dioxide
oxygen
nitrogen oxides
sulfur oxides
hydrochloric acid
"total hydrocarbon"
performance "indicator" species (e.g., CO)

Procedures for measuring the above parameters in ultimate effluents from MSW combustion facilities (stack gas, solid residues such as bottom- and fly-ash, and liquid effluents such as scrubber water) are described in this report. Two other aspects of MSW combustor sampling and analysis--measurements on the MSW feed and measurements on flue gases upstream of air pollution control devices--are also addressed, but procedures appropriate for these media are less well developed or defined. In both cases, the principal difficulty is in obtaining a representative sample. MSW is highly heterogeneous and some individual items present are so large or bulky as to preclude effective use of compositing procedures. (See Section IIIE for further discussion). Flue gas sampling (discussed in Section IIIC) is complicated by uneven flow conditions and by components (e.g., high particulate material and acid gas loadings) that clog or corrode conventional sampling equipment.

This document speaks only to issues of MSW combustor source sampling and analysis. Procedures for assessing ambient air impacts, either by dispersion modelling or by direct ambient air sampling and analysis in the vicinity of the facility, are not described. Sampling and analysis of fugitive emissions (e.g., from transfer or storage operations) are not covered in this document.

D. USE OF REPORT

It is anticipated that this report will serve as a useful reference point for MSW combustor owner/operators and for federal, state and local authorities involved in facility permitting process. The sampling and analysis methods described and/or recommended here are not to be construed as representing unique or mandatory requirements for emissions testing or continuous monitoring at MSW combustion facilities. Inclusion in this report does not mean that a sampling or analysis method is an official EPA method. The procedures described here should be reviewed against those in the current Code of Federal Regulations and in official methods manuals, such as "Test Methods for Evaluating Solid Waste" (SW-846)(1), before any MSW combustor test program is finalized.

II. SAMPLING AND ANALYSIS STRATEGIES

A. PURPOSE OF DATA COLLECTION

The principal purpose of generating data from MSW combustor sampling and analysis is to determine the effects of emissions from a facility on health and the environment. These data can be used to determine compliance with applicable criteria or to perform an assessment of the health risk associated with the emissions. In some cases, the purpose of the sampling and analysis may be primarily to support research and development in MSW combustion technology. In those instances, there may be a requirement for some types of measurements (e.g., characterization of waste feed or in-furnace measurements) that are more extensive than those needed for compliance testing or risk assessment.

Table 1 indicates some examples of the types of compounds for which measurements have been made in various test programs. Most of these are not regulated pollutants in stack gas emissions, and inclusion in the Table is not meant to imply that measurement of these potential pollutants should be required. However, this document presents methods that would be applicable to the sampling and analysis of these types of pollutants if such measurement were determined to be necessary or useful.

In every case, it is essential that critical decision limits for each parameter be established in specific quantitative terms prior to selection of sampling and analysis methods. This may require, in many cases, that a preliminary air quality modelling run be performed in order to calculate what stack gas concentration corresponds to a specific ambient air quality criterion. This exercise allows calculation of the sampling and analysis method detection limit that will be necessary to meet the project objectives.

The precision and accuracy criteria for the measurement method will also depend on the specific uses to be made of the data. It is important to establish whether it is each of n measurements, or the mean of n measurements,

TABLE 1

EXAMPLES OF POLLUTANTS THAT HAVE BEEN OF INTEREST IN RESEARCH AND DEVELOPMENT OR OTHER SPECIAL PURPOSE PROGRAMS

Volatiles:	Benzene	Metals:	Arsenic
	Carbon Tetrachloride		Beryllium
	Chloroform		Cadmium
	Formaldehyde		Chromium
	Perchloroethylene		Copper
	Toluene		Lead
			Manganese
			Mercury
			Nickel
			Selenium
Semivolatiles:	Benzo(a)pyrene	Others:	Hydrogen Chloride
	Chlorobenzenes		Hydrogen Fluoride
	Chlorodibenzodioxins		Sulfur Dioxide
	Chlorodibenzofurans		
	Chlorophenols		
	Naphthalene		
	Phenol		
	Polychlorinated Biphenyls		
	Pyrene		

Source: Arthur D. Little, Inc., conversations with regulatory authorities.

or the 95% confidence limit around the mean that is to be compared with the critical decision limit.

The general purposes of collecting data by testing and monitoring of MSW combustors are discussed below. The specific purposes (and thus the critical decision limits) must be established on a case-by-case basis.

Criteria Pollutants. The criteria pollutants (particulate material, carbon monoxide, nitrogen oxides, ozone, and sulfur dioxide) are those species for which EPA has established primary and/or secondary National Ambient Air Quality Standards (NAAQS). As the name implies, these standards apply to the cumulative impact from all sources, not the source-by-source emissions, on ambient air concentrations. However, it may be necessary to measure emissions of criteria pollutants from an MSW combustor in order to assess its incremental contribution to the total ambient level. This is especially likely in the case of new MSW facilities in areas where current levels are close to or exceed the NAAQS. The criteria pollutants are also of concern with regard to Prevention of Significant Deterioration (PSD) determinations.

Acid Gases. In addition to SO_x (discussed above), hydrochloric acid and a lesser quantity of hydrogen fluoride are acid gases that can be expected to be present in MSW combustor off-gases. Although there are not federal EPA standards relating to HCl emissions from facilities other than hazardous waste incinerators, many state environmental agencies (e.g., Maine, Massachusetts, New Jersey, California) consider that acid gas removal from MSW incinerator effluents represents Best Available Control Technology (BACT). Testing of stack emissions of HCl and HF may be required to demonstrate that a degree of acid gas control consistent with BACT has been achieved.

Trace Metals. Trace metal species, in addition to lead, that may need to be measured in MSW incinerator effluents include: arsenic, beryllium, cadmium, chromium, and mercury. In general, air emissions of trace metals from MSW sources are not currently addressed in EPA regulations, but may be of concern with regard to potential health effects. In some cases, it may be necessary to differentiate Cr (III) from Cr (VI) in order to assess the magnitude of health effects. The metals content of MSW incinerator aqueous effluents (e.g., scrubber or quench water) and of solid residues (e.g., bottom ash, fly ash) may need to be ascertained in order to determine disposal status vis-a-vis NPDES or RCRA regulations, respectively.

Organic Pollutants. Data on chlorinated dibenzo-p-dioxins and dibenzofurans in stack gas effluents may be required as inputs to air quality models in order to estimate whether the risk of exposure to these chemicals from this source is within the range of acceptability. Permitting authorities may request data on other trace organics such as polynuclear aromatic hydrocarbons or phenols, in order to perform similar risk calculations. Again, NPDES or RCRA regulations may require the determination of specific organic chemicals in aqueous effluents or solid residues, depending on the disposal or treatment alternatives that are to be applied to these streams. Selected organics may also be measured during MSW combustion research and development as indicators of the efficiency of the combustion process and/or pollution control devices.

Monitoring. Continuous monitoring of MSW combustor emissions provides a mechanism for tracking the performance of the system in real time. The parameters that can be monitored continuously are generally those (e.g., temperature, oxygen, carbon monoxide) that indicate the overall combustion efficiency or those (e.g., opacity, SO_x) that indicate air pollution control device (APCD) performance. These measurements are important for confirming that a facility is continuing to operate under controlled, steady-state conditions and is in compliance with specific emissions limitations written into its operating permits. In addition, the on-line monitor data can serve as an "early warning system" to detect combustor/APCD system upsets due to mechanical failures and/or gross changes in waste composition (e.g., very wet waste). Thus, even if an on-line monitor is not sufficiently accurate or precise for determining compliance with emissions limitations (e.g., commercially available opacity meters do not reliably determine particulate matter emissions below 0.03 gr/dscf), data from such an instrument is nevertheless useful as an indicator of potential upset conditions.

B. SELECTION OF SAMPLING AND ANALYSIS METHODS

Once the uses of the data have been defined and the consequent data quality objectives have been established, it is possible to make an informed selection among alternative sampling and analysis (S/A) methods.

The principal criteria to be used in making this selection are the following:

- regulatory status. Is the S/A method chosen approved by EPA for this measurement purpose?

- sensitivity. Has the method been proven to have a detection limit that is sufficiently low to allow accurate quantification of the pollutant of interest at concentrations corresponding to the critical decision limit?

- selectivity. Will other species that are likely to be present in MSW combustor effluents interfere in the determination?

- reliability. Is the method sufficiently rugged to be applicable in the hostile environment represented by MSW incineration?

It is important to emphasize that these criteria must be applied to the overall sampling--sample preparation--analysis system, not just to the analysis method *per se*.

C. QA AND QC OVERVIEW

Quality Assurance (QA) and quality control (QC) are vitally important components of any sampling and analysis program. QC procedures, including the analysis of standards, blanks, replicate samples, and spikes, provide on-going confirmation that the sampling and analysis methods are "in control" and that the data generated are valid for the intended purpose. QA procedures ensure that all data, including QC data, are reviewed and that any necessary corrective actions are instituted in a timely fashion.

In order to ensure the effective implementation of QA/QC functions, it is necessary that specific quantitative Data Quality Objectives (DQOs) be established for each measurement. Guidance in developing a QA/QC plan for MSW combustion testing/monitoring is discussed further in Section VII of this report and in the EPA report, "Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans."(2)

III. SAMPLING

A. OVERVIEW

Sampling of MSW combustion facilities for purposes of determining compliance with regulatory limitations or of assessing potential environmental risks is usually focused primarily on air emissions (stack gas). Solid residues (bottom ash and fly ash) are also commonly sampled. Some facilities may also have aqueous effluents from wet scrubbing or ash quenching operations.

Figure 1 shows a generalized schematic of the MSW combustion process, with sampling points indicated generically, Figures 2, 3, and 4 present, respectively, schematics of a mass burn, refuse-derived-fuel (RDF), and starved air MSW incinerator, again with generic identification of sampling locations. Exact sampling points must be specified on a case-by-case basis for each facility, taking into account accessibility, temperature and flow conditions, and operational modes (e.g., batch or continuous discharge of residue).

The critical considerations in selection of a sampling method are: (1) the representativeness of the sample and (2) compatibility of the sampling procedure with the intended analytical finish.

To ensure representativeness, emissions samples are usually integrated over time. A 1-4 hour time-integrated sample is usually taken to smooth out the perturbations that occur due to the inherent variability of MSW. In the case of stack sampling, it is often possible to accomplish this directly by adjusting the sampling rate to cover the desired time period. In the case of liquid or solid residues from MSW combustors, the time integration is usually accomplished by preparing a composite sample, combining equal-sized aliquots collected at intervals over the duration of a test. Sampling of solid waste, if requested in a particular facility test, is usually done by compositing of subsamples, in accordance with procedures described in SW-846. In all cases, the representativeness of the sampling method can be checked, but not proven, by acquiring duplicate samples representing the same time period of facility operation.

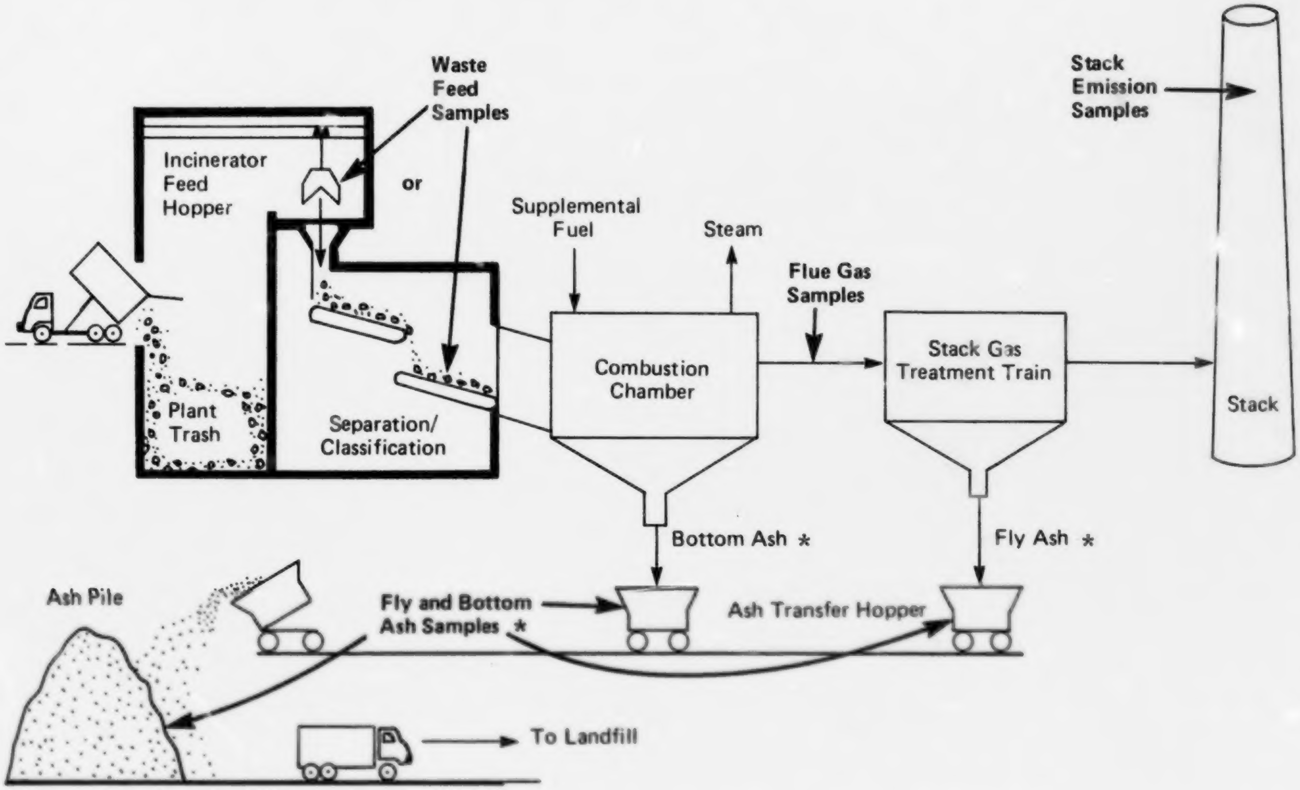
Waste
Feed
Samples
or
Incinerator
Feed
Hopper
Plant
Trash
Separation/
Classification
Supplemental
Fuel
Steam
Flue Gas
Samples
Combustion
Chamber
Stack Gas
Treatment Train
Stack Emission Samples
Stack
Bottom Ash *
Fly Ash *
Ash Pile
Fly and Bottom
Ash Samples *
Ash Transfer Hopper
To Landfill

FIGURE 1 GENERALIZED MUNICIPAL SOLID WASTE INCINERATION PROCESS SCHEMATIC

(Adapted from original by S-Cubed, a Division of
Maxwell Laboratories, Inc.)

*In many facilities, fly ash and bottom ash are collected in a single hopper.

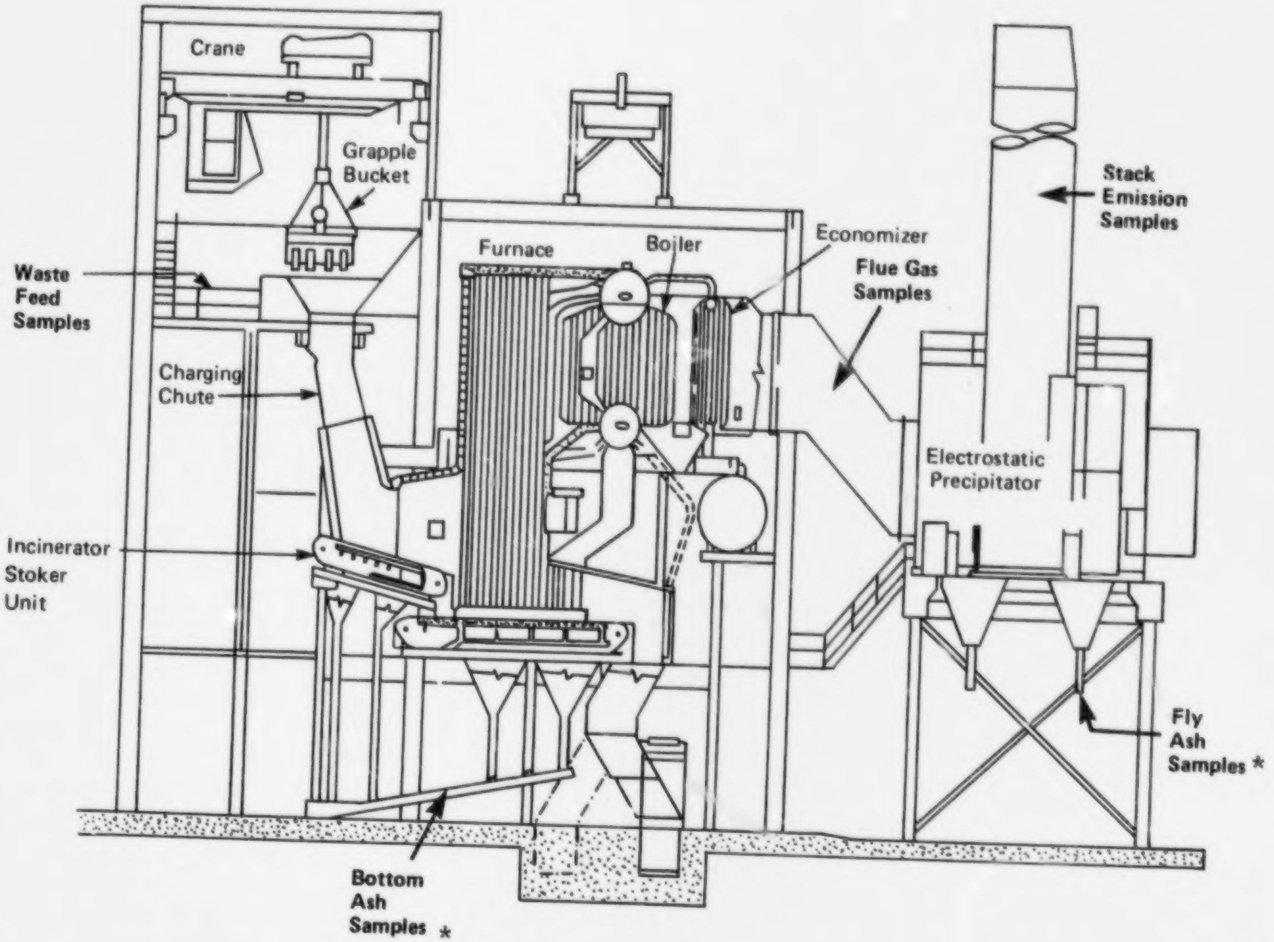
Crane
Grapple Bucket
Waste Feed Samples
Charging Chute
Incinerator Stoker Unit
Furnace
Boiler
Economizer
Flue Gas Samples
Stack Emission Samples
Electrostatic Precipitator
Fly Ash Samples *
Bottom Ash Samples *

FIGURE 2 **SIMPLIFIED SCHEMATIC OF A MASS BURN MSW COMBUSTOR, SHOWING SAMPLE LOCATIONS**
(Adapted from original by C. R. Brunner, "Incineration Systems Seminar," (1982))

*In many facilities, fly ash and bottom ash are collected in a single hopper.

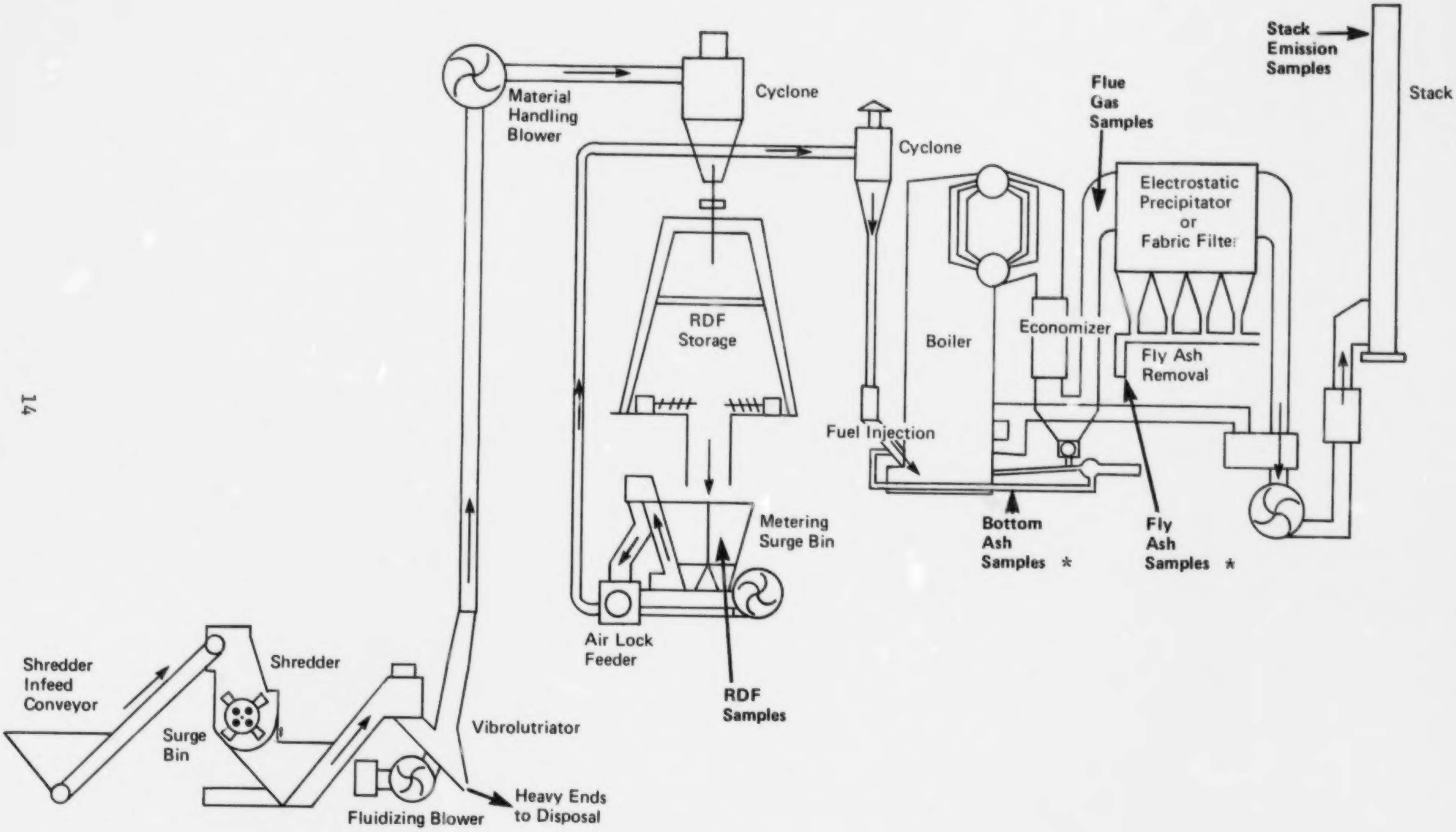
Shredder
Infeed
Conveyor
Surge
Bin
Shredder
Fluidizing Blower
Heavy Ends
to Disposal
Vibrolutriator
Material
Handling
Blower
Cyclone
RDF
Storage
Air Lock
Feeder
Metering
Surge Bin
RDF
Samples
Cyclone
Fuel Injection
Boiler
Economizer
Bottom
Ash
Samples *
Flue
Gas
Samples
Electrostatic
Precipitator
or
Fabric Filter
Fly Ash
Removal
Fly
Ash
Samples *
Stack
Emission
Samples
Stack

FIGURE 3 SIMPLIFIED SCHEMATIC OF AN RDF MSW COMBUSTOR, SHOWING SAMPLE LOCATIONS
(Adapted from original by C. R. Brunner, "Incineration Systems Seminar," (1982))
*In many facilities, fly ash and bottom ash are collected in a single hopper.

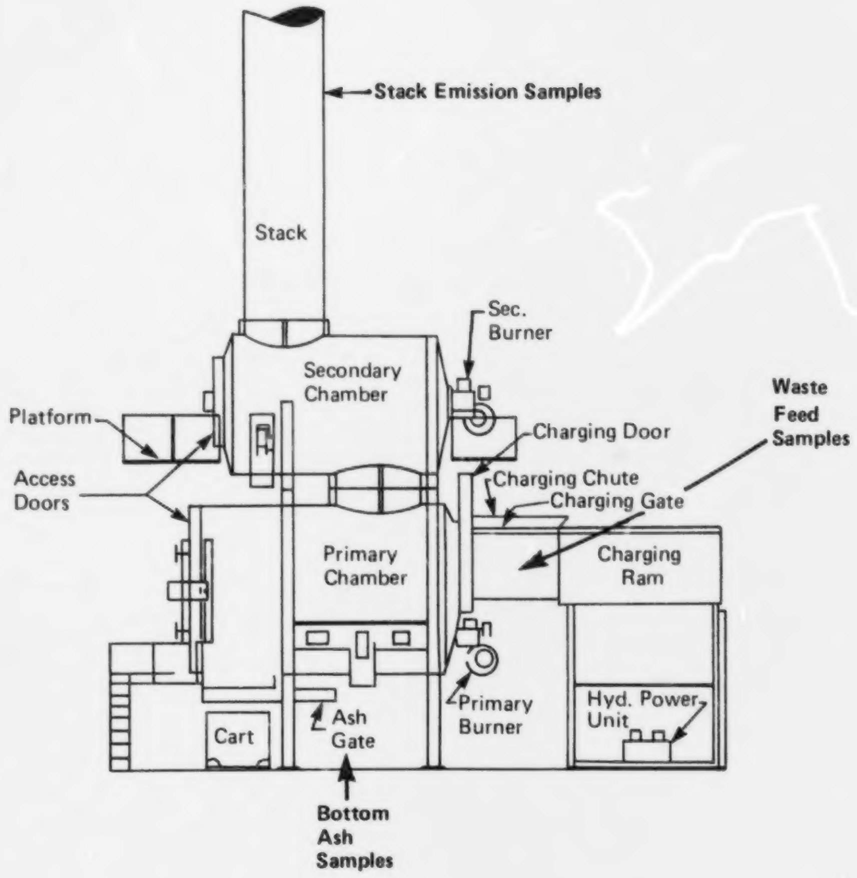
Stack Emission Samples
Stack
Sec. Burner
Secondary Chamber
Waste Feed Samples
Platform
Charging Door
Access Doors
Charging Chute
Charging Gate
Primary Chamber
Charging Ram
Primary Burner
Hyd. Power Unit
Ash Gate
Cart
Bottom Ash Samples

FIGURE 4 SIMPLIFIED SCHEMATIC OF A STARVED-AIR MSW COMBUSTOR, SHOWING SAMPLING LOCATIONS
(Adapted from original by C. R. Brunner, "Incineration Systems Seminar," (1982))

Compatibility is a complex issue. Most analytical methods (e.g., GC/MS for trace organics, AAS for trace metals) cannot be applied directly to the sample but require extensive sample preparation. Even methods that are inherently "on-line" procedures (e.g., continuous instrumental monitoring of CO or SO_x) may require sample clean-up to remove particulate material, water vapor, etc. or other forms of sample conditioning prior to analysis. It is important that the QAPP (quality assurance project plan) for any MSW combustion sampling and analysis program contain procedures to assure that no unacceptable losses are introduced by whatever procedures are required to ensure compatibility.

B. SAMPLING METHODS FOR STACK GAS EMISSIONS

Table 2 lists EPA-approved and/or recommended state-of-the-art stack sampling methods for various pollutants and/or categories of pollutants. (Note: Table 2 includes only extractive sampling methods. Continuous monitoring methods are discussed in Section VI.) Most of these procedures have been subjected to extensive method development, validation and/or round-robin collaborative testing. Although they may not all have been validated at MSW combustion facilities specifically, there is every reason to believe that they will be directly applicable for the purpose of sampling MSW stack emissions.

In fact, a number of these methods have been employed in recent MSW combustion sampling and analysis programs(3,4) and appear to provide reliable data. For example, Table 3 shows the results obtained in a series of 6 replicate stack gas emission tests for polychlorinated dioxins and furans at one MSW combustor using the ASTM sampling and analysis protocol(5) (see below and Appendix B for description).(6) These data show the precision (relative standard deviation (RSD)) that can be achieved when sampling and analysis is carried out according to the recommended methods by experienced personnel (in this case, Radian Corporation for sampling and Triangle Laboratories for analysis). The RSD values in the table reflect the combined effects of actual variations in emissions, sampling variance, and sample preparation/analysis variability for this test series. RSD's could be expected to be somewhat higher at lower PCDD/PCDF emission levels. However, the data indicate that the state-of-the-art sampling and analysis methods are workable in experienced hands. It should be

TABLE 2

STACK SAMPLING METHODS

Pollutant	Principle	Comment	Reference
Criteria and Conventional Parameters			
Particulate	Isokinetic collection of a 1 hr. sample on glass fiber filter at 120± 14°C. Train includes: T-controlled probe, optional cyclones, heated filter, impingers, flow control and gas volume metering system.	Designed to meet 0.08 gr/SCF standard. Probably adequate down to 0.01 gr/SCF, especially if sampling period is increased to 2 hrs.	EPA Meth. 5
	Visual determination of opacity		EPA Meth. 9
	Instrumental measurement of opacity (optical density)	Not reliable for quantification at 0.03 gr/SCF or below.	-
Sulfur Oxides	Collection in isopropanol (SO_3) and hydrogen peroxide (SO_2) impingers of M5-type train.	Low ppm to percent	EPA Meth. 6,8
Carbon Monoxide	Integrated gas bag or direct interface via air-cooled condenser.	Water vapor, carbon dioxide are interferences; need silica gel, ascarite traps to remove. 20-1000 ppm	EPA Meth. 10
Nitrogen Oxides	Collection in evacuated flask containing sulfuric acid and hydrogen peroxide.	Grab sample (not time-integrated) ppm levels Does not differentiate NO from NO_2	EPA Meth. 7,7A

TABLE 2 (cont.)

STACK (FLUE GAS) SAMPLING METHODS

Pollutant	Principle	Comment	Reference
Hydrochloric Acid	Collection in aqueous NaOH impingers in M5-type train.	ppm to percent range.	(18)
Hydrogen Fluoride	Collection on paper or membrane (not glass fiber) filter and aqueous impingers in M5-type train.	Low ppm range.	EPA Meth. 13B
Trace Metals			
General	M5 or SASS train, glass fiber filter and nitric acid or ammonium persulfate impingers	ppb to ppm levels if is ^ 0.75 M^3 of stack gas	(18)
Lead	Collection on glass fiber filter and nitric acid impingers in M5-type train.		EPA Meth. 12
Mercury	Collection in iodine monochloride or acidic permanganate impingers in M5-type train.	Probe must be glass- or quartz-lined. ppm levels. Other reagents also possible.	EPA Meth. 101
Arsenic	Collection on glass fiber filter and aqueous impingers in M5-type train.		EPA Meth. 108
Beryllium	Collection on millipore AA filter and aqueous impingers in M5-type train.	Probe must be glass or quartz-lined.	EPA Meth. 104

TABLE 2 (cont.)

STACK (FLUE GAS) SAMPLING METHODS

Pollutant	Principle	Comment	Reference
Trace Organics			
Specific Volatile organics	Collection on Tenax-GC and charcoal at 1 LPM for 20 minutes.	ppb-ppm levels;multiple species	VOST
Semi-volatile organics, including dioxins, furans	M5 train modified to include XAD-2 trap for organic collection between filter and impingers.	ppb-ppm levels; multiple species	MM5
	5-fold scale up of MM5 system.	sub-ppb levels for dioxins/furans if dedicated sample	SASS
Vinyl chloride*	Integrated gas bag	0.1-50 ppm	EPA Meth. 106
Formaldehyde	Collection on DNPH-coated sorbent or in aqueous DNPH impingers.	ppm levels	(18)
Gaseous Hydrocarbons, total	Integrated bag sample or direct interface	ppm levels	EPA Meth. 18
Gaseous Hydrocarbons, total	Evacuated stainless steel or aluminum tank behind chilled condensate trap.		EPA Meth. 25

* VOST can also be used for vinyl chloride, but collection and recovery efficiency may be low.

TABLE 3

Data from 1986 Test as Saugus Resource Recovery Plant

STACK GAS (Corrected to CO_2 12%)

	Avg conc (n = 6 MM5 runs) ng/dscm	sd	rsd
DIOXINS			
2,3,7,8	1.73	0.65	38
tetras	32	12	38
pentas	35	12	34
hexas	35	10	30
heptas	30	12	38
octa	37	26	68
Subtotal	169	49	29
monos			
dis	1	1	60
tris	12	5	37
Total	183	51	28
FURANS			
2,3,7,8	23	5	23
tetras	182	49	27
pentas	106	31	29
hexas	69	20	29
heptas	36	14	38
octa	18	25	139
Subtotal	411	101	25
monos	1	1	95
dis	31	8	25
tris	136	26	19
Total	579	126	22
GRAND TOTALS, DIOXINS + FURANS			
Cl4-Cl8	580	145	25
Cl1-Cl8	762	169	22

recognized that these procedures require an exceptionally high level of quality control to ensure that adequate recoveries and detection limits have been achieved in each instance.

The Method 5 (M5) type train represents the principal method for sampling of criteria pollutants, acid gases, metals, and semi-volatile organics. The basic Method 5 train, shown schematically in Figure 5, includes a probe with buttonhook nozzle and pitot tube, a filter section, an impinger train and a metering system. The probe and filter sections are maintained at a temperature of 250°F; material recovered from these train components and dried to constant weight is defined as particulate material. For quantification or chemical analysis of particulate material, the sampling must be done isokinetically (i.e., gas velocity into the probe equals the gas velocity within the stack).

As noted in Table 2, the M5 train is used with minor modifications to determine many inorganic species, such as sulfur oxides or trace metals. These modifications do not involve substantial changes in train geometry but relate to the use of: glass- or quartz probe liners; special filter media; or selective reagents in the M5 impingers. For example, use of a glass lined probe, glass fiber filter and 0.1 N nitric acid in the impingers of a standard M5 train provides good collection efficiency for most trace metals. To quantify heavy metals in the stack emissions, the probe catch, filter and/or impinger solutions are digested as described in Section IV G and analyzed as described in Section V D.

For sampling of semivolatile organics in stack emissions, a more significant modification of the standard M5 train is required. The Modified Method 5 (MM5) train (SW-846 method 0010), shown in Figure 6, incorporates a condenser/cooler section and a module filled with a solid adsorbent between the exit of the filter and the entrance to the first impinger. The adsorbent recommended is Amberlite XAD-2, which has been shown(7,8) to give good collection efficiency for vapor phase organic compounds with boiling points above about 100°C. This category, "semivolatile" organics, includes many species that are of potential interest for risk assessment (Table 1), including chlorobenzenes, chlorophenols, polycyclic aromatic hydrocarbons, and chlorinated

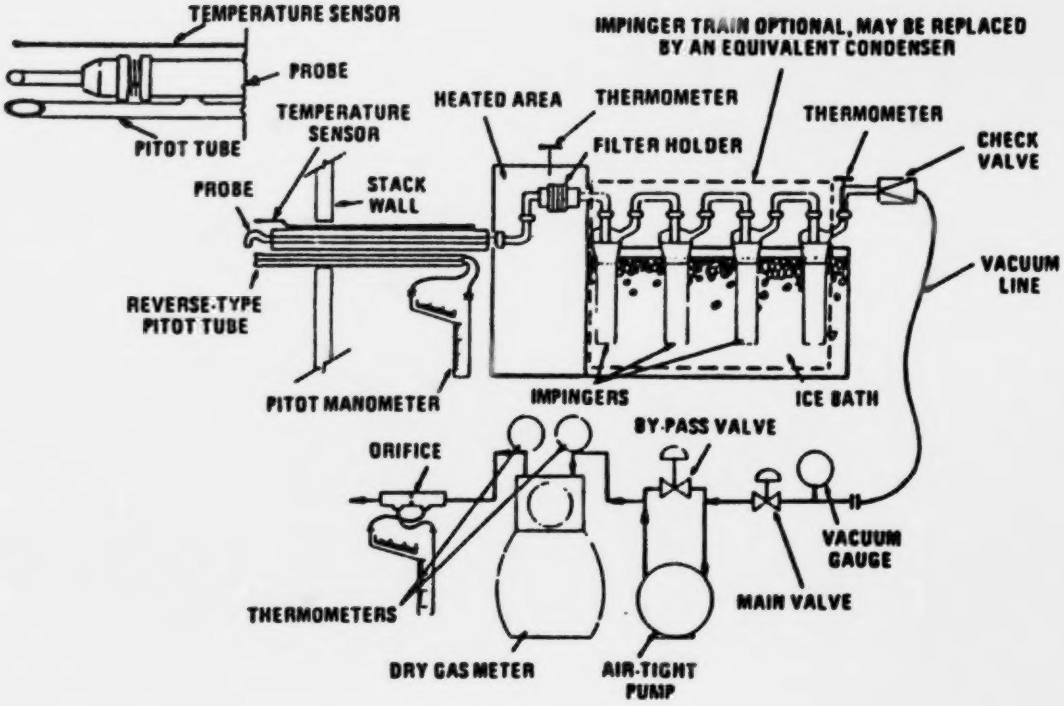
TEMPERATURE SENSOR
PROBE
PITOT TUBE
TEMPERATURE SENSOR
PROBE
STACK WALL
REVERSE-TYPE PITOT TUBE
PITOT MANOMETER
HEATED AREA
THERMOMETER
FILTER HOLDER
IMPINGER TRAIN OPTIONAL, MAY BE REPLACED BY AN EQUIVALENT CONDENSER
THERMOMETER
CHECK VALVE
VACUUM LINE
IMPINGERS
ICE BATH
ORIFICE
BY-PASS VALVE
VACUUM GAUGE
MAIN VALVE
THERMOMETERS
DRY GAS METER
AIR-TIGHT PUMP

FIGURE 5 SCHEMATIC OF STANDARD EPA METHOD 5 TRAIN.

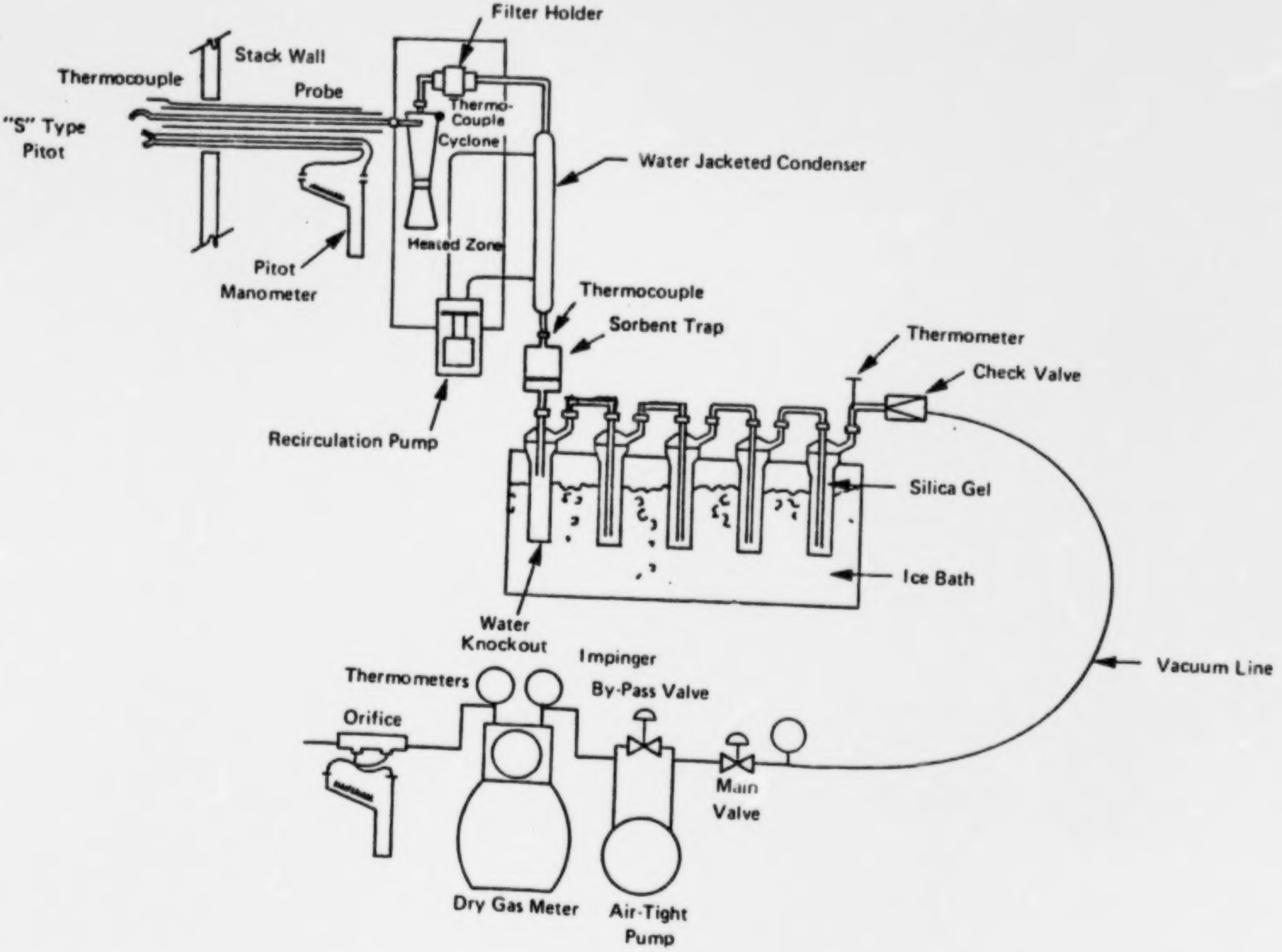
Filter Holder
Stack Wall
Thermocouple
Probe
"S" Type Pitot
Thermo-Couple
Cyclone
Water Jacketed Condenser
Heated Zone
Pitot Manometer
Thermocouple
Sorbent Trap
Thermometer
Check Valve
Recirculation Pump
Silica Gel
Ice Bath
Water Knockout
Impinger
Vacuum Line
Thermometers
By-Pass Valve
Orifice
Main Valve
Dry Gas Meter
Air-Tight Pump

FIGURE 6 MM5 TRAIN SCHEMATIC DIAGRAM

dibenzodioxins/furans. The MM5 train is recommended for sampling of dioxins/furans in MSW combustion effluents in the joint ASME/EPA Environmental Standards Workshop draft Protocol.(5) (See Appendix B.) The MM5 approach has also been used by other agencies involved in sampling for dioxins/furans, including the New York State Department of Environmental Conservation (9) and Environment Canada (10). There are some differences in configuration between the MM5 train designs currently in use; these may produce somewhat different distribution of collected pollutants across the train components (i.e., different fractional collection on filter vs. sorbent vs. condensate). However, all contain the same basic components and should provide comparable overall collection efficiencies.

The MM5 train, like the M5 train, is used to sample isokinetically. Also, as with the M5, a variety of impinger reagents can be used for selective collection of species such as trace metals (Table 2).

The Source Assessment Sampling System (SASS) (SW-846 method 0020) is an alternative to the MM5 train. The SASS, shown schematically in Figure 7, is essentially a fivefold scale-up of the MM5 system. Use of SASS is recommended when calculations indicate that the sampling flow rate of the M5/MM5 train (0.75-1.0 cu. ft. per min.) would not collect a sufficient quantity of pollutant in a reasonable time period to meet data quality objectives for detection limits. Note that the design criteria for the SASS train cyclones are based on a constant sampling rate, not on a variable rate as used in true isokinetic sampling. The SASS may therefore be most suitable for sampling semi-volatile organics and trace metals that are present in the stack as vapor phase materials. The variation from isokineticity may introduce errors when the SASS is used to collect particulate material; however, the variations and any resultant errors are generally small compared to other sources of variance in an MSW combustor sampling and analysis program.

The operation of both the MM5 and the SASS train is described in reference 11. Note that each of these stack sampling trains generates multiple components for subsequent sample preparation and analysis (Sections IV and V). Note also that, while the M5-type approach can be modified to meet a number of sampling

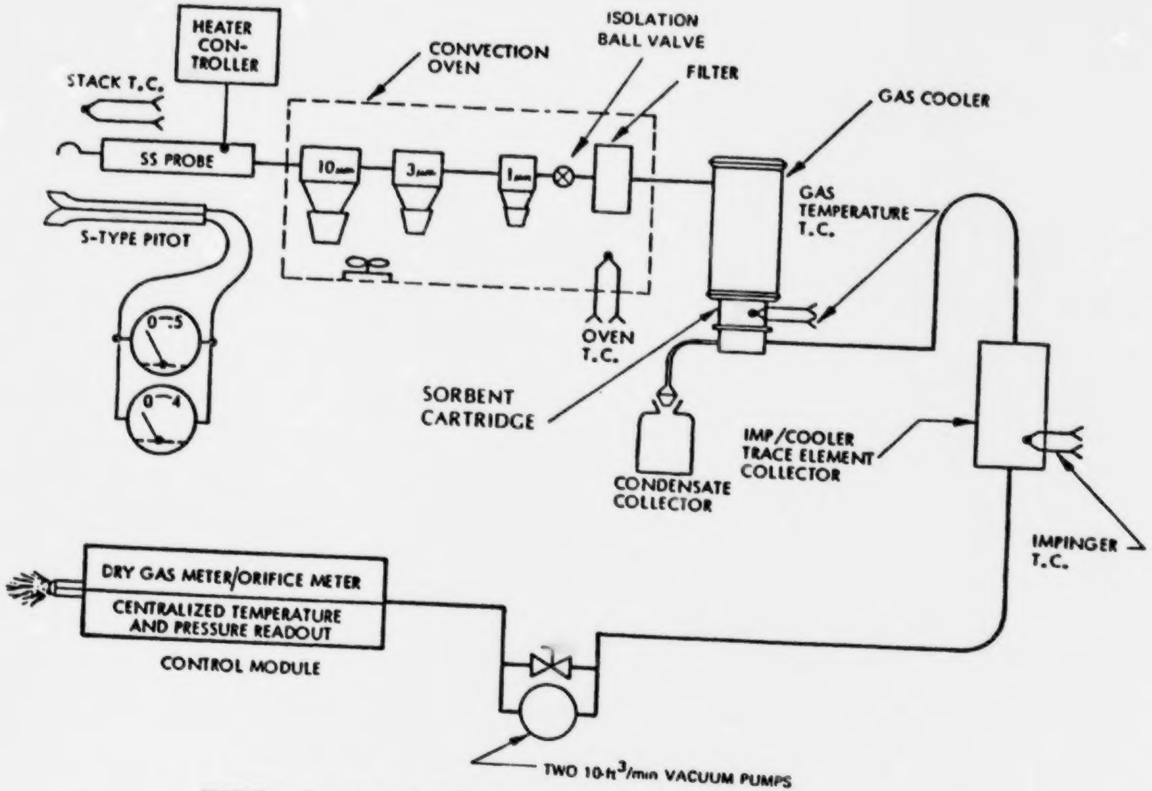
HEATER CON- TROLLER
STACK T.C.
SS PROBE
S-TYPE PITOT
0–.5
0–4
CONVECTION OVEN
10μm
3μm
1μm
ISOLATION BALL VALVE
FILTER
OVEN T.C.
GAS COOLER
GAS TEMPERATURE T.C.
SORBENT CARTRIDGE
CONDENSATE COLLECTOR
IMP/COOLER TRACE ELEMENT COLLECTOR
IMPINGER T.C.
DRY GAS METER/ORIFICE METER
CENTRALIZED TEMPERATURE AND PRESSURE READOUT
CONTROL MODULE
TWO 10-ft³/min VACUUM PUMPS

FIGURE 7 SASS SCHEMATIC DIAGRAM

Source: TERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition), EPA-600/7-78-201 objectives (particulate material, trace metals, semi-volatile organics, acid gases), it is generally recommended that one not attempt to meet more than one (or two) of these goals with a single stack sample. In theory, for example, one could run a MM5 train, dry the probe wash and filter to constant weight for weighing of particulate material, then split the particulate catch--digesting one-half for trace metal determination and extracting the other half for semi-volatile organic analysis. In practice, such an approach is likely to result in sample losses and in unnecessarily high limits of detection for particular pollutants.

The Volatile Organic Sampling Train (VOST) was developed(12) to sample organic vapors that are too volatile for efficient collection in the MM5 or SASS. This includes most organics with boiling points of about 100°C or lower. This includes a number of species that may be of interest such as carbon tetrachloride, benzene and vinyl chloride. A schematic of the VOST is shown in Figure 8. As shown, the VOST system includes a probe, glass wool roughing filter, a gas cooling/condensing section, and two solid adsorbent tubes in series. The first tube contains 1.6g of Tenax-GC® sorbent and the second contains 1.0g of Tenax backed up by 1.0g of charcoal. The VOST is used to collect a series of 20L stack gas samples at a flow rate of 1 LPM through 5 successive pairs of fresh traps. After sampling, the tubes are sealed and returned to the laboratory for thermal desorption and analysis of volatiles by GC/MS (Section V). A protocol for use of VOST has been published by EPA(13) and is also available in SW-846 as method 0030(1).

The VOST system has been extensively validated in the laboratory(12) and applied successfully in the field(14). In addition, EPA has sponsored the development and testing of a series of VOST audit cylinders, containing known mixtures of volatile organics, that are available to regulatory agencies as checks on overall VOST sampling and analysis performance by users of the system.

C. SAMPLING METHODS FOR FLUE GAS

The methods described in Section B, above, are also applicable to sampling of flue gases upstream of air pollution control devices (APCDs). However, flue

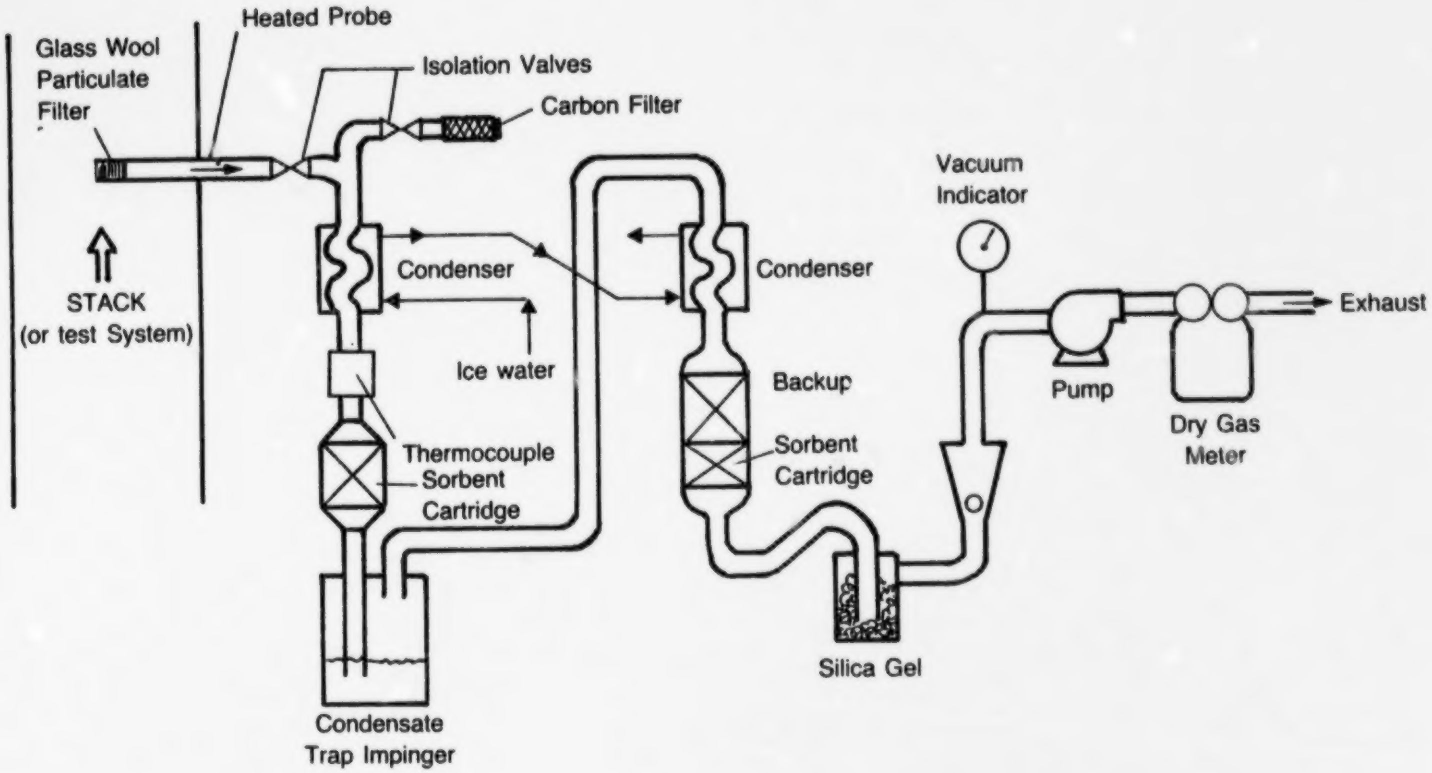
Glass Wool
Particulate
Filter
Heated Probe
Isolation Valves
Carbon Filter
STACK
(or test System)
Condenser
Ice water
Thermocouple
Sorbent
Cartridge
Condensate
Trap Impinger
Condenser
Backup
Sorbent
Cartridge
Silica Gel
Vacuum
Indicator
Pump
Dry Gas
Meter
Exhaust

FIGURE 8 SCHEMATIC OF VOLATILE ORGANIC SAMPLING TRAIN
(VOST)

gas is typically hotter, wetter, dirtier (higher particulate loadings, higher levels of condensable organics) and more corrosive than stack gas. Thus modifications are frequently required to adapt stack gas methods to flue gas sampling. For example:

- When the flue gas temperature is in excess of about 500°C, a water-cooled jacket must be placed around the outside of the heated probe.
- The flow conditions within the flue and difficulty in accessing sampling points may preclude isokinetic sampling and/or traversing of the duct. A preliminary velocity traverse will usually allow selection of a fixed sampling point of "average" velocity that is away from the walls of the flue. The probe can then be located at this position and the sampling rate adjusted to be as close to isokinetic as practical.
- High loadings of particulate material and/or condensable organics may cause frequent interruptions of sampling for replacement of filters to avoid excessive pressure drops across the train. Use of a roughing filter (in-flue) or insertion of a cyclone component upstream of the M5-type filter may be necessary to allow reasonably convenient continuity of sampling.
- Glass, quartz, or Teflon liners may be required to protect all stainless steel surfaces from corrosion.

The principal reason for sampling the flue upstream of the APCD is to allow assessment of control device removal efficiency. An alternative approach is to sample and analyze the material collected in the device, rather than the flue gas challenge concentration, and compare this to the quantity emitted in the stack gas. The efficiency can then be estimated as:

$$E(\%) = \frac{Q_{collected}}{Q_{collected} + Q_{emitted}} \times 100$$

where $Q_{collected}$ - concentration in fly ash x rate of fly ash collection in APCD

$Q_{emitted}$ - concentration in stack gas x volume flow rate of stack gas

This "mass balance" is probably comparable in uncertainty to that based on direct flue gas measurements for "major" pollutants in MSW combustion, such as particulate material or acid gases. It cannot be recommended for trace level pollutants such as individual metals or organics.

D. SAMPLING METHODS FOR SOLID AND LIQUID EFFLUENTS

The methods specified in SW-846(1) and in "Sampling and Analysis for Hazardous Waste Combustion (First Edition)"(15) are generally directly applicable to MSW combustor solid and liquid effluents. Table 4 summarizes the relevant methods. In addition, EPA is currently in the process of developing specific recommendations for sampling MSW combustor ash.

For both liquid and solid effluents, the sampling strategy will depend on whether the stream is generated continuously (as in once-through scrubber water) or in a batch process (as in a fabric filter). In the former case, composite samples are generated by collecting equal-sized aliquots at regular time intervals over the course of the test run (e.g., from a tap on a discharge line (liquid) or from a conveyor (solid).) In the latter case, composite samples are prepared from subsamples from statistically selected points that represent the horizontal (area) and vertical (depth) extent of the batch.

Particular problems may be encountered in sampling MSW combustor bottom ash, which may include bulky items such as metal containers. This issue should be specifically addressed in the sampling and analysis plan for each test. It must be recognized that any decision to "sample around" such bulky objects could compromise the overall validity of the data collected, unless it could be established that they are negligible sources of the compounds to be determined.

TABLE 4

SAMPLING METHODS FOR SOLID AND LIQUID EFFLUENTS*

Stream	Principle	Method
Liquids in pipelines.	Attach TFE line to tap. Flush container with fresh sample, then fill.	Tap
Liquids in sumps, tanks, or open drain.	Glass or TFE beaker on rod.	Dipper
Wet or dry ash on conveyors or in bins.	Stainless steel trowel or lab scoop. Obtain random sample below surface level.	Scoop
Dry fine ash on conveyors, in bins or piles.	Tube within a tube, rotated to align slots for sampling.	Thief
Wet ash in bins or piles.	Section of tube cut in half lengthwise. Insert into waste and withdraw.	Trier

*Reference 1

E. SAMPLING METHODS FOR WASTE FEED

This stream is grossly inhomogeneous. None of the sampling techniques promulgated for hazardous waste sampling (SW-846)(1) is directly applicable to MSW as-received at a mass-burn combustion facility. (Some refuse-derived-fuel (RDF) processes may produce a waste stream that is sufficiently homogeneous and finely divided to be amenable to scoop or trier/thief sampling.)

Researchers have chosen one of two approaches towards sampling MSW: stratified random sampling at the source (socio-economic demography)(16) or by subjectively-modified random sampling at the repository, be it an incinerator or a landfill(17,18,19). For purposes of evaluating the performance of an MSW combustor, or of understanding the relationship between emissions and waste feed characteristics, the latter is the preferred approach.

Procedures used for sampling and testing of refuse, and the resulting variability in measurements of properties of MSW, have been summarized by Hasselriis (20). Based on this review, it is recommended that 3 to 10 samples of MSW should be collected over at least a 2 week sampling period. The smallest sample should be 1 "unit" of MSW (i.e., one trash bag or barrel of domestic waste at the source; one truck hopper load or crane bucket load at an MSW combustor plant. Cone and quarter procedures can be applied to reduce the unit to a manageable sample size (80-130 kg); this sample can then be shredded to achieve a reasonably homogeneous material for analysis. As an example, the MSW sample processing protocol reported by Bell(16) is included in Appendix A. If any element of subjective sampling is imposed (e.g., exclusion of bulky items or hospital wastes) this must, at a minimum, be explicitly noted and an estimate of the quantity of rejected material be provided.

The EPA, Department of Energy(DOE), and American Society for Testing of Materials (ASTM) have been collaborating in the development of protocols for RDF sampling, including sampling accuracy, bias, and reproducibility estimates. A draft procedure has been approved by an ASTM subcommittee and is awaiting ballot approval by the main E-38 Committee on Resource Recovery. This protocol should be a useful resource for designing waste sampling plans for MSW combustors in general.

IV. SAMPLE PREPARATION PROCEDURES

A. OVERVIEW

The sample preparation procedures for use on MSW combustor samples involve a number of steps. In the field, the collected samples must be transferred to appropriate, clean containers (generally glass or TFE for organic analysis and high-density linear polyethylene for inorganic analysis) and appropriately preserved and stored. In the laboratory, the sample must be converted (via digestion, extraction, etc.) into a matrix which is compatible with the final analysis methods needed. Table 5 presents a summary of the sample preparation procedures that will commonly be required for MSW combustor samples. This table indicates how samples collected by procedures in Section III are converted to forms amenable to analysis by procedures in Section V.

In some cases (e.g., analysis of chloride in caustic impinger solutions) the sample preparation may be minimal (e.g., diluting an aliquot to a known volume). In other cases (e.g., analysis of dioxins/furans in an MM5 stack gas sample) the procedures may be complex, requiring extraction of multiple components, concentration and clean-up of extracts.

The use of surrogate or standard addition methods is strongly recommended as a QC check on any losses in the sample preparation steps. For this purpose, the additions should be made to the sample prior to any sample preparation.

B. REPRESENTATIVE ALIQUOT FROM FIELD SAMPLES

Combination and preparation of representative aliquots of collected samples is appropriate for all MSW combustor solid and liquid effluent samples. The collected sample is homogenized prior to withdrawal of aliquots for analysis. Individual aliquots are composited to form a single sample (or replicate QC samples) for subsequent preparation and analysis procedures. Table 6 summarizes these procedures.

TABLE 5

SUMMARY OF SAMPLE PREPARATION METHODS

MSW Combustor Stream	Sample Type	For Analysis Of	Preparation Procedure	Cross References*		
				Sampling	Prep	Analysis
Stack Gas	M5, MM5 or SASS					
	- probe wash - filter	Particulate	Dry to constant weight	III B	-	-
	- probe wash - filter - impinger solutions	Metals	Standard addition to split samples. Digest in acidic oxidizing medium	III B	IV G	VD
	- probe wash - filter - sorbent module	Semivolatile organics	Add surrogate. Soxhlet extract with CH_2Cl_2. Concentrate. Clean-up as necessary	III B	IV C-F	VD
	- condensate	Semivolatile organics	Add surrogate Liquid-liquid extract at pH 2 and pH 11 with CH_2Cl_2. Concentrate. Clean-up as necessary	III B	IV C-F	VD
	VOST - sorbent cartridges	Volatile organics	Spike with internal standard. Thermally desorb onto analytical trap. Desorb this trap into GC/MS.	III B		VD
	- condensate	Volatile organics	Spike with internal standard. Purge onto analytical trap. Desorb into GC/MS.	III B		VD

TABLE 5

SUMMARY OF SAMPLE PREPARATION METHODS (cont.)

MSW Combustor Stream	Sample Type	For Analysis Of	Preparation Procedure	Cross References*		
				Sampling	Prep	Analysis
Flue Gas	M5, MM5, SASS	(same as for stack gas)		III C		
	VOST					
Bottom Ash and Fly Ash	Composite Grab	Metals	Standard addition to split samples. Digest in acidic medium in Parr bomb.	III D	IV G	VD
		Semi-volatile organics	Add surrogate. Soxhlet extract with CH_2Cl_2. Concentrate. Clean-up as necessary.	III D	IV C-F	VD
Liquid Effluents	Composite Grab	Metals	Standard addition to split samples. Digest in acidic, oxidizing medium.	III D	IV G	VD
		Volatile Organics	Spike with internal standard. Purge onto analytical trap. Desorb into GC/MS.	III D	IV G	VD
		Semivolatile Organics	Add surrogate. Liquid liquid extract at pH 2 and pH 11 with CH_2Cl_2. Concentrate. Clean-up as necessary.	III D	IV C-F	VD

TABLE 5

SUMMARY OF SAMPLE PREPARATION METHODS (cont.)

MSW Combustor Stream	Sample Type	For Analysis Of	Preparation Procedure	Cross References*		
				Sampling	Prep	Analysis
Waste Feed	Composite Grab		Grind or mill to reduce particle size. Take subsamples.	III E		
		Metals	Same as for ash samples.		IV G	VD
		Semivolatile Organics			IV C-F	VD
		Volatile** Organics	Spike with internal standard. Dilute in reagent water or polyethylene glycol in purge cell. Purge, trap and desorb into GC/MS.			VD

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*Cross references are to sections of this document.

**Reference: Miller, N.C., R.W. James and W.R. Dickson, "Evaulated Methodology for the Analysis of Residual Waste," Report prepared under EPA Contract No. 68-02-1685 (December 1980). Also see SW-846 method 8240.

TABLE 6

SUMMARY OF PROCEDURES FOR COMPOSITING SAMPLES

Physical Form	Homogenizing	Compositing	Minimum Quantity of Composited Sample
Aqueous	Shake well and pour aliquot	Combine aliquots in clean container and shake to mix well.	1 L (semi-volatile organics) 1 L (metals)
	NOTE: For volatiles analysis, composite just prior to analysis by adding aliquots from multiple VOA bottles to purge cell.		5 mL (volatile organics)
Sludges/ Slurries	Stir or shake well; use dipper to take > 3 portions.	Combine aliquots in clean container and stir or shake to mix.	100 mL (semi-vol organics) 100 g (metals)
Solids	Grind, if necessary, to reduce particle size (20 mesh screen) using agate or alumina equipment; riffle through steel or aluminum riffler.	Combine aliquots, cone-blend three times, roll-blend, cone and quarter.	50 g (organics) 100 g (metals)

Samples of stack (flue) gas collected with an extractive sampling train (M5, MM5, SASS or VOST) already represent time-averaged sample collections. In effect, the sampling approach has composited the gas on a time-weighted basis. It is generally inappropriate to further composite such samples. However, in some cases where ultra-low levels of detection are required (e.g., dioxin/furan analysis), it may be necessary to pool the entire extracts from multiple sampling runs.

C. RECOVERY METHODS

The specific sampling methods listed in Table 2 contain explicit procedures for the physical recovery of samples from the train. However, they do not necessarily specify procedures for monitoring the chemical recovery achieved in the sample preparation process. There are two basic approaches that can be used for this purpose: (1) addition to each sample of surrogate compounds, which are chemically similar to the species of interest but not expected to be present in the sample (e.g., for GC/MS analyses, stable isotope-labelled analogs of the target compounds); or (2) standard addition (spiking) of the target species themselves to selected split samples.

The spiking levels used in each instance are selected after consideration of the target detection level for each analyte and the expected concentration of the species in the sample. For MSW incinerator effluent samples, it is generally desirable to select spiking levels that correspond to 2 to 10 times the target detection limit or to 2 to 4 times the critical decision limit. The level chosen should be explicitly stated in the QAPP for each test program.

For example, assume that the critical decision limit for a semi-volatile organic pollutant (e.g., 2, 3, 7, 8-teterachlorodibenzodioxin, TCDD) is 1 ng/m^3 in stack gas, and a 5 m^3 sample of stack gas is to be collected using the MM5 train. An appropriate level of surrogate (e.g., $^{13}C_{12}$-2, 3, 7, 8-TCDD) to be spiked into the MM5 train components prior to extraction can be calculated as:

$$4 \times 1 \text{ ng/m}^3 \times 5 \text{ m}^3 = 20 \text{ ng surrogate}$$

Assuming that the organic extract is concentrated to a final volume of 1.0 ml, and that 5 μL are injected into the GC/MS system, this spiking level would yield 100 pg of surrogate on-column if recovery through the sample preparation steps were 100%, and 50-pg on column if recovery were only 50%. It must be confirmed by analysis of calibration solutions that these levels are within the analytical detection limit of the GC/MS system. Recovery of 60% or higher can be expected(21) if the laboratory procedures are under control.

D. EXTRACTION METHODS

Solvent extraction with methylene chloride is the procedure most broadly used to prepare samples for organic analysis. In the case of stack sampling trains, several separate extractions (of probe wash and filter, sorbent trap, and of condensate) will be required. It is general practice to combine these extracts prior to analysis so that a single value is obtained for the stack gas concentration of each species. This approach allows lower detection limits to be achieved. Further, there is no intrinsic advantage to differentiating between material collected in the "particulate" (front half) vs "vapor" (back half) portions of the train, since these catches do not necessarily indicate the particulate/vapor distribution present in the stack(4,22,23).

Liquid-liquid extraction, using a manual, separatory funnel method or a continuous extractor, applies to: (1) spent scrubber water or other waste water effluent from the MSW combustor and (2) aqueous condensate collected from the stack gas effluent in the MM5 or SASS trains. The volumes of sample/extracting solvent and any necessary pH adjustment of the sample should be as specified in EPA Method 625 if the purpose of data collection is NPDES compliance determination. In the case of stack gas condensate, these parameters can be scaled down to accommodate the actual quantity of sample collected.

Soxhlet extraction applies to: (1) solid effluents from the MSW combustor and (2) probe wash, filter and sorbent components of the MM5 or SASS trains. Quantities of sample and extraction solvent should be as specified in Method P024 b (Sampling and Analysis for Hazardous Waste Combustion)(15) or Method 3540 (SW-846).(1)

Some very wet ash samples or sludges may require alternative extraction procedures (e.g., homogenization, Methods P022 a,b or P024 a,c).(15) Also, solid or slurry samples that are not suitable for direct introduction to the purge cell of a purge-and-trap apparatus may require a micro-extraction (e.g., Methods P022b, P024c)(15) prior to determination of volatiles.

If the MSW combustor test program includes evaluation of solid residues vis-a-vis the RCRA hazardous waste characteristics, a separate sample of the solid material must be extracted by the EP (Method 1310, SW-846) or the new TCLP (Fed. Reg. Vol. 51, No. 114, June 13, 1986), when promulgated as a final method.

E. DRYING AND CONCENTRATING OF EXTRACTS

Unless an alternative procedure is specified in a particular analytical procedure, solvent extracts should be passed through a short column of anhydrous sodium sulfate into a Kuderna-Danish evaporative concentrator apparatus. In most cases, rapid concentration to a final extract volume of 1-10 mL will provide adequate detection limits without unacceptable losses of semi-volatile organic species.

F. SAMPLE CLEAN-UP

For some samples, the level of interfering compounds is sufficiently high to preclude successful analysis for the species of interest. For such samples, one or more clean-up steps must be included in the sample preparation procedures Because of the wide variation in sample matrices and in the physical/chemical properties of the species that may be sought, no single method or set of methods can be recommended for MSW combustor samples. This is one of the reasons why use of surrogate spiking of MSW combustor samples is strongly recommended (Section IV C). If it can be demonstrated that recovery and detectability of the surrogate are adequate, then no clean-up steps are necessary. However, if interferences overload the analytical column or detector and the surrogate is not detectable, clean-up will be required. This must be established empirically for each project. The QAPP should specify the criteria for acceptable surrogate recovery/detectability and corrective actions to be taken if the criteria are not met.

Some analysis methods (e.g., Methods 8010-8250, SW-846(1)) specify that silica gel, Florisil or alumina column clean-up be applied. In some cases three or more sequential clean-up steps may be required. For example, the ASME methodology for analysis of dioxins and furans(5) specifies sequential passage of the concentrated sample extract through 1) a combination column containing silica gel and acid and base-modified silica gel, 2) a basic alumina column, 3) a PX21 carbon/celite 545 column and 4) a silica/diol column. Such an extensive clean-up is usually not necessary unless the critical decision limit is in the ng/mg^3 range. However, using at least one column clean-up step (silica gel, alumina) may significantly improve detection limits when critical concentrations are in the $\mu g/m^3$ range.

G. DIGESTION

The preparation method for all samples requiring metals analysis includes a digestion step. Its purpose is to convert all of the metal-containing species into inorganic form.

For most sample types, an acidic, oxidizing medium is specified for digestion. Solid samples can be digested using HF and HNO_3 in a Parr bomb. Solutions can be digested using HNO_3 and H_2O_2(24). In some instances, repeated digestion using HNO_3 alone(1) may give adequate recovery. For mercury in solid materials, Method 105 (40 CFR Part 61) calls for aqua regia digestion followed by potassium permanganate oxidation.

A relatively new development is the use of microwave energy, rather than a conventional hot plate, for acid digestions. This reduces the time and acid quantity required for complete digestion(24).

V. ANALYSIS PROCEDURES

A. OVERVIEW

The overall strategy for analyzing samples from MSW combustion must reflect the multiple possible purposes of data collection discussed in Section II A.

When the purpose of the data collection is to determine compliance with a specific regulation concerning air, water, or solid effluents (or their disposal) it is essential that the analysis method used be one recognized by the appropriate agency. These include, but are not necessarily limited to:

EPA NSPS Methods 1-5	40 CFR Part 60
EPA NESHAPS Methods 101-108	40 CFR Part 61
EPA Clean Water Act Methods 601-612; 624, 625; 1624, 1625; 200.7	40 CFR Part 136
EPA RCRA Methods 7040-7951; 8010-8310	SW-846

One exception to the above generalization relates to measurement of criteria pollutants in combustor effluents. The EPA NAAQS methods for criteria pollutants are ambient air monitoring methods that are suitable for source monitoring only with modifications (gas conditioning; dilution). However, there are NSPS methods applicable to direct measurement of criteria pollutants in combustion sources.

Even when the purpose of data collection is to provide input for more general environmental assessment, or risk assessment, rather than regulatory compliance, the above EPA-approved methods are frequently useful. In particular, the nearly-identical GC/MS-based methods designed for determination of priority pollutants (624, 625; 1624, 1625) or Hazardous Substance List (HSL) compounds (RCRA 8240, 8250, 8270) have wide applicability for organic analysis.

The corresponding procedures for metals analysis by atomic absorbtion spectroscopy (AAS) or inductively coupled plasma spectroscopy (ICP) are also directly applicable to MSW combustor samples.

For some assessment purposes, official federal EPA methods may be inappropriate or unavailable. In these cases, methods promulgated by ASTM and ASME should be used if available. For example, there is at present no official method for determination of dioxin/furan congeners that applies specifically to MSW stack emission sample analysis. However, a procedure developed to support a joint ASME-EPA project on MSW combustion is recommended (5). In addition, SW-846 method 8280 may be used for homolog-specific analysis.

Similarly, there are presently no official methods suitable for screening MSW combustor samples to identify and/or quantify other pollutants that may be present as a result of incomplete combustion. Research in this area is underway as well. The selection of appropriate analysis methods for such pollutants must be established on a case-by-case. Part C of this section provides some preliminary suggestions.

Potentially useful methods for direct analysis of selected species in MSW combustor effluents using continuous instrumental monitors will be discussed in Section VI of the report.

B. PROXIMATE ANALYSIS

"Proximate analysis" is a term used in "Sampling and Analysis for Hazardous Waste Combustion (First Edition)"(15) to describe procedures for determining the approximate (gross) composition of hazardous waste. The methods recommended for that purpose include:

% moisture, solid and ash determination
elemental analysis (%C, N, S, P, F, Cl, Br, I)
total organic carbon
total organic halogen

heating value
viscosity

These methods are applicable to MSW.

C. SCREENING ANALYSIS

As noted above, screening analysis is intended to identify and/or quantify species that are present in a sample and are of potential concern with regard to effects on health and/or environment but were not specifically pre-selected for analysis (see Section D, Directed Analysis). There are no official procedures for screening analysis. In practice, the approach that has most commonly been used in research and development programs involving waste combustion has been as follows.

For organic species, perform full-mass range scanning (e.g., 40-500 amu) under appropriate GC/MS conditions (usually capillary column and El ionization). In most cases, the GC/MS conditions specified in EPA methods 624/1624/8240 for volatiles and in EPA methods 625/1625/8250/8270 for semivolatiles will be applicable to screening analysis of MSW combustor samples. In addition to providing data for directed analysis, the results of these analyses can be used to identify unknown or unexpected compounds by comparison to a library of reference spectra or by spectral interpretation. A typical criterion for screening analysis is to attempt to identify the 20 most intense unknown peaks or those peaks whose intensity exceeds 10% of the internal standard intensity (whichever is the lesser number of unknowns).

For inorganic species, ICP analysis can be used to screen for about 20-23 metals that are known or suspected to be of environmental concern. Alternative approaches sometimes recommended to address a broader range of elements include: X-ray fluorescence, neutron activation analysis, particle-induced X-ray emission, and spark source mass spectrometry. All of these are multielement methods and require minimal sample preparation. However, the instrumentation required is expensive and not widely available. Also, the methods are more amenable to qualitative screening than to quantification unless standards and samples are carefully matched to eliminate sample matrix effects.

It is probable that screening analysis is more likely to be requested for MSW combustor air emission samples than for liquid or solid effluents. These methods can be applied to samples of MSW combustor stack gas collected with the MM5, SASS or VOST (volatile organics only) after suitable sample preparation techniques have been applied. They should also apply to liquid or solid effluent samples after sample preparation.

D. DIRECTED ANALYSIS

As noted in the overview to this Section, analysis methods are available for most species that are likely to be pre-selected as targets for analysis in MSW incineration. Table 6 lists suitable analysis methods for organics and metals that may be of concern. Specific methods for distinguishing between species such as Cr (VI) and Cr (III), suitable for use with combustion effluent samples, based on selective extraction of Cr (VI) by an alkaline reagent, are under development and in the process of validation by EPA's Emission Measurement Branch at Research Triangle Park, North Carolina(25). In addition, SW-846 lists methods both for Cr(VI) and for total chrome; these methods are potentially applicable to MSW combustor samples providing that suitable procedures for solubilization of the chromium are applied.

Note that, for organic analysis, Table 7 lists only the GC/MS alternatives. Methods that use GC or HPLC with detection principals less specific than MS (e.g., flame ionization (FID) or electron capture (ECD) detection for GC, ultraviolet (UV) or refractive index (RI) for HPLC) are less likely to be useful for MSW combustion samples, because of the variety and quantity of potentially interfering substances likely to be present.

TABLE 7

ANALYSIS METHODS FOR TRACE ORGANICS AND TRACE METALS, APPLICABLE TO MSW COMBUSTOR SAMPLES

Species	Method	Reference
Volatile Organics	Packed column GC/MS; full mass range scanning 20-260 amu.	1, 15
Semivolatile Organics	Capillary column GC/MS; full mass range scanning 40-500 amu.	1, 15
Dioxins/Furans	Capillary column GC/MS; selected ion monitoring.	1, 5
Metals	Flame (high levels) or furnace (low levels) AAS.	1, 24
	Inductively coupled plasma spectroscopy (not for mercury, lead, arsenic)	1, 24

VI. CONTINUOUS MONITORING METHODS

A. OVERVIEW

Continuous monitoring systems include in situ measurements, in which a sensor is mounted directly in a stack or flue, and extractive methods, in which a sample of stack or flue gas is pumped through an interface to the measuring device. In situ monitoring offers the advantage that no alteration in flue gas composition is introduced by the system. Conversely, however, an in situ sensor must be physically resistant to stack conditions (temperature, moisture, particulate matter) and be chemically selective (blind to potential interferences). An extractive approach is amenable to gas sample conditioning to remove substances that might interfere with the desired measurement or damage the instrument. It also allows instruments to be placed in a sheltered location where maintenance and calibration are more convenient. However, this approach provides opportunity for loss of target species in transfer lines and in components of the gas conditioning system.

Many continuous monitors are based on rather sophisticated chemical analysis principles. Manufacturers have made considerable efforts to "ruggedize" the commercially available systems so that they are capable of unattended operation for periods of days to weeks and can be maintained/calibrated by plant operating personnel. Despite these advances, it is vital that a rigorous QA/QC program be established for continuous monitors to ensure that misleading data are not recorded and that operating problems are not overlooked.

B. SAMPLE CONDITIONING

An extractive sampling system interface typically includes the following components:

- probe
- coarse filter
- transfer lines

- pump
- moisture removal system
- fine filter

The probe must be located at a point in the stack or flue that allows a representative sample to be withdrawn. A multi-port probe may be useful in this regard. Depending on stack or flue temperature and corrosivity, materials of construction may be stainless steel or ceramic. The coarse filter, usually located in-stack to minimize effects of condensation, is typically sintered metal or ceramic, depending on temperature. Ceramic is more resistant to high temperature corrosion effects but also more susceptible to cracking. Plugging of the probe and/or coarse filter can be a severe problem, especially when sampling flue gas upstream of particulate control devices. Backflushing the system regularly with clean carrier gas may help but frequent replacement of the in-stack filter will probably still be required.

The transfer lines must be constructed of inert materials that are resistant to corrosion and do not absorb the species to be measured; ceramic (probe) and Teflon® are materials of choice for most applications. Stainless steel would be an alternative if the stack or flue gas is not highly corrosive. The pump must also be constructed of, or coated with, inert material such as Teflon®. Especially when samples are to be monitored for organics, any potential contamination of the sample with lubricants must be avoided. Diaphragm or bellows pumps can meet this constraint.

Moisture removal can be accomplished in several ways: adsorption (e.g., silica gel); condensation; dilution to below dew point; membrane permeation system. Issues that must be addressed in selection of the drier component include: adequate capacity for water removal given the moisture content of the stack or flue gas; and minimal coincident losses of target species along with the water. A condensation approach, for example, may lead to unacceptable losses of acid gases such as HCl and SO_x.

The fine particulate filter is usually located close to the analyzer inlet. It usually must achieve virtually complete removal of all particles larger than

1 micron. When sampling flue gases, these filters require replacement whenever the pressure drop across the filter approaches the limit of pumping capacity.

C. MONITORS FOR INORGANICS

The following is based on information provided by instrument suppliers and by references 26 and 27.

Continuous temperature measurements in combustor flue or stack gases are generally accomplished by using type J, K, or RT thermocouples. The thermocouples must be shielded from radiation and protected against mechanical damage and corrosion by shielding inside a ceramic or metal protection tube or in a thermowell.

Continuous monitoring of particulate material is generally accomplished using an in situ opacity meter. Typically, these devices measure changes in optical density, OD (percent transmittance), due to scattering and/or adsorption of light by particles in the stock. The OD reading obtained depends not only on the mass loading of particulates that are present, but also on their size distribution, the particle shape, particle composition, the system's temperature, the presence or absence of water droplets and the configuration of the stack. The lack of measurement specificity may render opacity monitors less reliable at MSW combustors than at other stationary sources, as waste feeds at MSW locations are highly variable, probably causing emission levels and compositions to vary over time as well. Also, commercially available opacity meters for stack monitoring may be uncertain by a factor of two or more at particulate loadings below 0.03 gr/SCF.

Extractive sampling, rather than in situ monitoring, is most commonly used for inorganic gases, although in situ monitors are available for CO, CO_2, O_2, NO_x, and SO_x. Typically, the detection of pollutant species of concern is accomplished using one of the detection principles identified in the descriptive information presented below. There is relatively little history of application of these instruments to MSW combuster stack gas and, especially, flue gas.

However, they have been used for continuous monitoring at other types of stationary sources.

Non-Dispersive Infrared (NDIR)

Perhaps the most common detection principle used by continuous analyzers is nondispersive infrared (NDIR). Amenable for use in the determination of CO, CO_2, NO_x, and SO_x, detection by NDIR is based on the principle that each of these pollutants, and many others, will absorb specific signature wavelengths of infrared light. Thus, by generating matched beams at the correct signature wavelength, passing one through a clean "reference" cell while the other is passed through a cell containing sample gas, and determining the difference in the intensity between the twin beams, it becomes possible to measure the amount of a particular pollutant species that is present.

Generally, detection is accomplished using devices such as a thermistor, a thermocouple, or a microphonic device.

The principle advantages of NDIR based instrumentation is the fact that it is comparatively low in cost and that the technology is applicable to a wide variety of pollutant species. Also, instruments are relatively rugged and commercially available systems have been in use in field monitoring situations for many years. Problems that are associated with this detection principle are that there are other chemical species that will absorb similar signature wavelengths of infrared light, and the fact that optical systems needed to produce, transmit, and receive the generated infrared light may degrade due to contact with the sample gas.

Non-dispersive Ultraviolet

Non-dispersive ultraviolet (NDUV) analyzers employ much the same philosophy as do the analyzers based on NDIR absorbtion, only in this instance, the light source emits in the ultraviolet or visible regions of the spectrum and a reference cell is generally not used. Typically, a reference wavelength in a region where the pollutant species of interest has minimal absorptive capacity is generated and quantitation is completed by differential analysis.

An important advantage of the NDUV analyzers is that water vapor is not an interference, as water does not absorb light in the ultraviolet region of the spectrum. As is the case with most extractive monitoring techniques, however, particulates which will absorb or scatter generated light must be removed from the sampled gas stream.

Polarographic Analyzers

Numerous pollutant species of potential interest at MSW combustors may be measured continuously using polarographic analyzers. Polarographic analyzers operate on the principle of selective diffusion and chemical reaction of a pollutant species of interest which induces a current flow that is measured electronically. The sensing device intrinsic to the operation of all polarographic analyzers is commonly called the electrochemical transducer.

In operation, the pollutant species of interest enters the transducer through a selective, semi-permeable membrane. Once in the transducer, the pollutant is oxidized or reduced by reaction with an electrolyte solution which induces a current flow. The induced current flow is proportional to the concentration of the pollutant species in the gas stream. The selectivity of electochemical transducers is dependent upon the selection of membrane materials, electrolyte, and sensing electrode chemistry or composition.

The polarographic analyzers offer several advantages over other analyzers, including multi-pollutant capability by switching transducer, fast response and simplicity of operation. Principle disadvantages of this technique are that transducers must be replaced or rejuvenated periodically, and the instrument must be frequently calibrated because the response of the transducer does deteriorate as the electrolyte solution is consumed.

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Electrocatalytic Analyzers

Electrocatalytic analyzers are currently available for oxygen determination. This type of instrumental determination is based on the principle that current flow is induced when two solutions containing similar materials at differing concentrations are brought into contact. Thus, by having two cells, one a reference and the other the unknown, separated by a porous zirconium oxide barrier (acting as both an electrolyte and catalyst), an electron current flow can be promoted, measured, and related directly to oxygen content.

Paramagnetic Oxygen Analyzers

Oxygen content may also be determined using a paramagnetic analyzer. Detection in a paramagnetic analyzer utilizes the fact that oxygen molecules (and the molecules of a few other compounds) are attracted by a magnetic field.

Two different philosophies of paramagnetic detection are commonly used in instrumentation. One, called thermomagnetic or magnetic wind instruments are based on the principle that the magnetic attraction of oxygen decreases as temperature increases. The second, called magneto-dynamac, uses the paramagnetic attraction of oxygen to swing a specialty torsion balance.

Chemiluminescence

Certain inorganic pollutants, most notably nitrous oxide and ozone, may also be detected using analyzers based on chemiluminescence. Within this type of instrumentation, the pollutant species of interest is mixed with a second reactant to generate light. Ideally, the generated spectrum of light produced is specific only to the pollutant of interest, but more commonly, optical means are used to isolate and quantitate the intensity of specific wavelength. By measuring the intensity of the generated light, a direct estimate of the concentration of pollutant species present in the gas sample may be obtained.

Information of currently available instrumentation for inorganic pollutant species in MSW combuster exhausts are presented in Tables 8 through 14.

TABLE 8

Continuous Analyzers for Carbon Monoxide

Detection Principle	Ranges	Interferences	Comments	Examples
Nondispersive Infrared	0-50 PPM 0-100 PPM 0-200 PPM 0-1000 PPM 0-5000 PPM 0-1 % 0-5 %	Water Vapor and Particulates; other species with similar infrared absorbance characteristics	In-situ or remote; Water Vapor and Particulates should be removed; corrosive gases may etch optics	Anarad, Inc. Dynatron Horiba Infrared Ind. Rosemont (Beckman) Servomex Siemens
Polarographic (Electrochemical)	0-50 PPM 0-100 PPM 0-250 PPM 0-500 PPM 0-999 PPM 0-4 %	Unsaturated Hydrocarbons and ammonia	Requires sample conditioning to remove particulate and reduce temperature	Energetics Science Interscan Neotronics Sensidyne

TABLE 9

Continuous Analyzers for Carbon Dioxide

Detection Principle	Ranges	Interferences	Comments	Examples
Nondispersive Infrared	0-10 PPM 0-100 PPM 0-500 PPM 0-2500 0-5000 PPM 0-0.5 % 0-2.5 % 0-5 % 0-20 % 0-100 %	Water Vapor and Particulates; other species with similar infrared absorbance characteristics	In-situ or remote; Water Vapor and Particulates should be removed; corrosive gases may etch optics	Anarad, Inc. Dynatron Horiba Infrared Ind. Rosemont (Beckman) Servomex Siemens Syconex Corp.
Polarographic (Electrochemical)	0-50 PPM 0-100 PPM 0-250 PPM 0-500 PPM 0-999 PPM 0-4 %	Unsaturated Hydrocarbons and ammonia	Requires sample conditioning to remove particulate and reduce temperature	Sensidyne

TABLE 10

Continuous Analyzers for Oxygen

Detection Principle	Ranges	Interferences	Comments	Examples
Polarographic (Electrochemical)	0-1 % 0-5 % 0-10 % 0-25 % 0-35 % 0-100 %		Gas must be cooled and particulate removed	Horiba MSA Neutronics Servomex
Electrocatalytic	0-10 % 0-22 %		Good for high temperature application	Anarad, Inc. Dynatron Lynn Products MSA Servomex Westinghouse
Paramagnetic	0-1 % 0-5 % 0-2.5 % 0-10 % 0-25 % 0-50 % 0-100 %			Horiba Rosemont (Beckman) Siemens

TABLE 11

Continuous Analyzers for Sulfur Dioxide

Detection Principle	Ranges	Interferences	Comments	Examples
Nondispersive Infrared	0-500 PPM 0-2000 PPM 0-10000 PPM 0-1 % 0-5 % 0-10 % 0-30 % 0-100 %	Water Vapor and Particulates; other species with similar infrared absorbance characteristics	In-situ or remote; Water Vapor and Particulates should be removed; corrosive gases may etch optics; Generally selected for percent applications	Anarad, Inc. Dynatron Infrared Ind. Rosemont (Beckman) Siemens Syconex Corp.
Nondispersive Ultraviolet	0-50 PPM 0-100 PPM 0-500 PPM 0-1000 PPM 0-5000 PPM			Anarad, Inc. Teco
Polarographic (Electrochemical)	0-5 PPM 0-10 PPM 0-50 PPM 0-100 PPM	Methyl and Ethyl Mercaptans, Hydrogen Sulfide, Ammonia		Interscan

TABLE 12

Continuous Analyzers for Nitrogen Oxides

Detection Principle	Ranges	Interferences	Comments	Examples
Nondispersive Infrared (for NO only)	0-500 PPM 0-2000 PPM 0-10000 PPM 0-2 % 0-10 %	Water Vapor and Particulates; other species with similar infrared absorbance characteristics	Water Vapor and Particulates should be removed; corrosive gases may etch optics	Horiba Rosemont (Beckman) Siemens Syconex Corp.
Nondispersive Ultraviolet (for NO2 only)	0-50 PPM			Anarad Inc
Polarographic (Electrochemical) (for NO only)	0-25 PPM 0-50 PPM 0-250 PPM	Methyl Mercaptan, Ammonia, Nitrogen Dioxide, Sulfur Dioxide	Requires sample conditioning to remove particulate and reduce temperature	Energetics Science Interscan
Chemiluminescent	0-2.5 PPM 0-10 PPM 0-25 PPM 0-100 PPM 0-1000 PPM 0-2500 PPM 0-10000 PPM	Possible Ammonia, Carbon Dioxide, and Water	Need to dry and remove particulates from sample	Monitor Labs Rosemont (Beckman) Thermo Electron

TABLE 13

Continuous Analyzers for Hydrochloric Acid

Detection Principle	Ranges	Interferences	Comments	Examples
Nondispersive Infrared		Water Vapor and Particulates; other species with similar infrared absorbance characteristics	In-situ or remote; Water Vapor and Particulates should be removed; corrosive gases may etch optics	Flakt Syconex Corp Teco
Polarographic (Electrochemical)	0-5 PPM 0-10 PPM 0-20 PPM 0-50 PPM 0-200 PPM	Chlorine gas, Methyl and Ethyl mercaptan, Hydrogen Sulfide, Ammonia, Nitric Oxide, Hydrogen Cyanide, and Sulfur Dioxide	Requires sample conditioning to remove particulate and reduce temperature	Interscan

TABLE 14

Continuous Analyzers for Hydrogen Cyanide

Detection Principle	Ranges	Interferences	Comments	Examples
Polarographic (Electrochemical)	0-5 PPM 0-10 PPM 0-20 PPM 0-50 PPM	Chlorine gas, Methyl and Ethyl mercaptan, Hydrogen Sulfide, Ammonia, Nitric Oxide, Hydrochloric acid, and Sulfur Dioxide	Requires sample conditioning to remove particulate and reduce temperature	Interscan

D. MONITORS FOR ORGANICS

Total hydrocarbons (or total non-methane hydrocarbons) at ppm to percent levels in stack gases can be monitored continuously with a flame ionization detector (FID) or infrared (IR) detector. These detectors are relatively rugged and are quite sensitive to hydrocarbons. The response factor is generally lower for organics that incorporate functional groups such as halides, hydroxyl, carbonyl, carboxylate.

The photoionization detector (PID) is applicable to many of these organic categories, but experience with this detector as a continuous monitor is more limited. There is some evidence that maintenance is more of an issue with PID than with FID or IR instruments.

The electron capture detector (ECD), which has high sensitivity and selectivity for halogenated organics under laboratory conditions, is not rugged enough for routine continuous monitoring in the field. Also, because these detectors contain radioactive materials, NRC permitting regulations govern their installation and use. The Hall detector, also specific for halogenated species, has been used at hazardous waste incineration sites, but with difficulty.

Catalytic combustion (hot wire) and thermal conductivity detectors are also used for continuous monitoring of organics. However, most commercially available instruments based on these principles are generally designed for percent level concentrations corresponding to explosive limits of combustible gases and vapors. A few low-level instruments suitable for MSW combustion monitoring are available, however,

Monitoring of specific organic compounds, rather than total organics, requires that chromatographic separation be accomplished prior to detection, Instrumental monitors that interface a gas chromatograph to an FID or PID are commercially available. These operate in a semi-continuous basis, since the chromatographic separation imposes a cycle time of (typically) 5-30 minutes between measurements.. The GC/FID or GC/PID analyzers are vulnerable to false positive interferences because the retention time is an imperfect means of compound identification.

Instruments based on more selective detection principles (e.g., GC/MS or GC/FTIR) are beyond the present state-of-the-art for stack monitoring, except in research installations. Instruments using these detectors may be sufficiently expensive to install and demanding to operate that they are not suitable for routine continuous monitoring. Most require, for example, more stringent control of temperature, humidity and power supply than is likely to be practical at an operating MSW plant.

E. INDICATOR OR SURROGATE MONITORING

A conceptual ideal for continuous monitoring of MSW combustors would be a inexpensive, rugged, and simple instrument that provides continuous measurement of a surrogate parameter indicative of total system performance. Identification of a suitable surrogate parameter, which can be reliably correlated with emissions of any and all pollutants of potential concern, is one of the objectives of on-going research in MSW combustion technology. At the present time, the carbon monoxide level in the air emissions is generally regarded as the best available surrogate for chemically-based monitoring of overall combustion efficiency. Monitoring of combustion temperature is also relied on as an indicator that the process is in control. Methods for monitoring these indicator parameters are discussed in Section VI C.

F. SPECIAL QA/QC CONSIDERATIONS

All of the general provisions that will be discussed in Section VII apply to continuous monitoring. A few special considerations are worth noting, however.

First, calibration with zero and span gases should be performed on the system as a whole, not just on the analyzer/detector itself. This may, however, be literally impossible for _in situ_ monitors; generating a stack or flue full of calibration gas of known composition is not a realistic approach. In the case of extractive monitoring systems, provision should be made to allow introduction of calibration gas at, or just behind, the probe. This approach to "total system" calibration has been incorporated into all of the federally referenced continuous monitoring methodologies that are currently applicable to stationary sources.

The EPA has also established guidelines for instrumentation that is used to continuously monitor sulfur dioxide, nitrogen oxides, carbon dioxide, oxygen, and carbon monoxide emissions from stationary sources. These guidelines fall into two categories including both instrumental design criteria and performance specifications.

Instrumental design criteria establish minimum acceptable levels for items such as instrumental response time, interference rejection ratios and ranges. Performance specifications are established to assure that the developed data is accurate and precise. Specifications for calibration drift and the relative accuracy of calibration, as well as requirements for duration of unattended operation are established. Specific criteria applicable to monitors used to measure CO, CO_2, O_2, NO_x, and SO_x are provided in Title 40 Code of Federal Regulations, Part 60.13 and Appendix A and B.

Second, QA/QC procedures for continuous monitoring methods must take into account the fact that operating personnel may have had minimal training and experience with chemical measurements and analytical instrumentation. The procedures must, therefore, place minimum reliance on operator judgment and be as explicit and simple as possible concerning QC criteria and corrective actions.

Third, the question of data reduction and data maintenance for continuous monitor output deserves special consideration. A continuous monitor, in one sense, generates an infinite number of data points on pollutant concentration vs. time. It must be determined in advance whether daily, weekly, monthly, etc. data are to be archived and/or reported. Are running averages desired? Commercially available data loggers are able to conduct these functions once decisions are made with respect to these parameters. How should/must short-term excursions from average values be recorded/reported?

G. POTENTIAL FOR PROCESS CONTROL

The acquisition of continuous monitoring data affords opportunities for process control, either by operator intervention or by use of automatic feedback loops. In current MSW combustion practice operator intervention is the more common response mode, but newer facilities are moving toward more automated systems.

Catastrophic failure of the system (e.g., plugging of nozzles in a dry scrubber or breakage of a fabric filter) is generally readily detectable by operators even in the absence of continuous monitoring data. Temperature and, secondarily, oxygen data from continuous monitors can be (and are) used to adjust process operating parameters such as MSW feed rate or over/underfire air supply to the incinerator.

Use of chemical monitoring data for process control is more complicated, both in theory and in practice. In general, the relationship of MSW combustion operating conditions to the emission rates of pollutants, especially trace organics, is not well enough understood to allow systematic process control in response to monitoring data.

VII. QUALITY ASSURANCE AND QUALITY CONTROL

A. OVERVIEW

A vital part of any sampling and analysis program is the provision for procedures which maintain the quality of the data obtained throughout the sampling and analysis exercise. These procedures, termed quality assurance and quality control (QA/QC), serve to (a) document the quality (i.e., accuracy, precision, completeness, representativeness and comparability) of generated data; (b) maintain the quality of data within predetermined control limits for specific sampling and analysis procedures; and (c) provide guidelines for corrective actions if QC data indicate that a particular procedure is out of control.

The following definitions, which represent interdependent activities, serve to differentiate between the complementary activities of quality assurance and quality control.

- Quality Assurance (QA) activities addresses the delegation of program responsibilities to appropriate individuals, documentation, data review, and audits. The objective of the QA procedures is to allow an assessment of the reliability of the data.

- Quality Control (QC) activities address the maintenance of facilities, equipment, personnel training, sample integrity, chemical analysis methods, and production and review of QC data. QC procedures are used continuously during a sampling and analysis program to maintain the quality of data within control limits. QC data should be evaluated immediately by the analysts; if the QC data fall outside a set of specified control limits, corrective actions, as specified in the work plan, must be taken.

In this section, specific QA/QC procedures are described. For an individual sampling and analysis program, these procedures and/or others may be selected to reach the goal of obtaining high-quality data. At a minimum, the procedures which are selected must be consistent with the standard operating procedures and/or good laboratory practices of the sampling crew and analytical laboratory involved.

The following discussion of QA/QC procedures is based upon a guidelines document(2) issued by the Office of Monitoring Systems and Quality Assurance of the EPA Office of Research and Development. This document, QAMS 005/80, entitled "Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans," and the references cited therein provide an extensive resource in selecting appropriate QA/QC procedures for sampling and analysis efforts. The QAMS-005/80 document identifies sixteen essential elements of a QA Project Plan (QAPP). These elements are listed in Table 15 and described briefly in the following discussion. A QAPP of some kind would generally be required for most sampling and analysis efforts.

B. TITLE PAGE AND TABLE OF CONTENTS

These elements are self-explanatory. The title page should indicate individuals with QA responsibility for the sampling and analysis efforts. Approval signatures should be required prior to the start of the sampling and analysis efforts. The Table of Contents should include a distribution list for the QAPP.

C. PROJECT DESCRIPTION

A general description of the project, including the experimental design, and intended use of data should be provided. The description may be brief but should have sufficient detail to allow the individuals responsible for review and approval, of the QAPP to perform their task. Flow diagrams, tables and charts should be included, as appropriate. A schedule, with anticipated start and completion dates, should also be specified.

TABLE 15

ESSENTIAL ELEMENTS OF A QA PROJECT PLAN

1. Title Page
2. Table of Contents
3. Project Description
4. Project Organization and Responsibility
5. QA Objectives
6. Sampling Procedures
7. Sample Custody
8. Calibration Procedures and Frequency
9. Analytical Procedures
10. Data Reduction, Validation, and Reporting
11. Internal Quality Control Checks
12. Performance and System Audits
13. Preventive Maintenance
14. Specific Routine Procedures Used to Asses Data Precision, Accuracy and Completeness
15. Corrective Action
16. Quality Assurance Reports to Management

Source: U.S. Environmental Protection Agency/Office of Monitoring Systems and Quality Assurance, Office of Research and Development, Washington, D.C., "Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans," QAMS-005/80 (December 29, 1980)

D. PROJECT ORGANIZATION AND RESPONSIBILITY

A table or chart which shows the project organization and line authority should be included. An example project organization chart is shown in Figure 9. Key individuals who are responsible for ensuring the collection of valid measurement data and the routine assessment of measurement systems for precision and accuracy should be identified; the responsibilities of each individual should also be delineated. It should be noted that the QA coordinator should be organizationally independent of the project organization so that the risk of conflict of interest may be minimized.

E. QUALITY ASSURANCE OBJECTIVES

For each major measurement system, numerical QA objectives for accuracy, precision and completeness should be established. These objectives may be generally based on previous experience in applying comparable procedures to similar sample matrices as well as on the requirements of the program. The QA objectives for precision, accuracy and completeness should be summarized in a table or chart; an example of a summary table is shown in Table 16.

All measurements should be made such that results are representative of the media (e.g., waste feed, stack emissions) and conditions being measured. Any factors considered within the experimental design to ensure representativeness should be described.

All data should be calculated and reported in units consistent with other organizations reporting similar data to allow for comparability of data bases among organizations. Units for all measurement parameters should be specified.

F. SAMPLING PROCEDURES

A detailed description of all sampling procedures to be used is an integral part of any QAPP. Where applicable, the following information should be included:

- Description of techniques or guidelines used to select sampling sites.

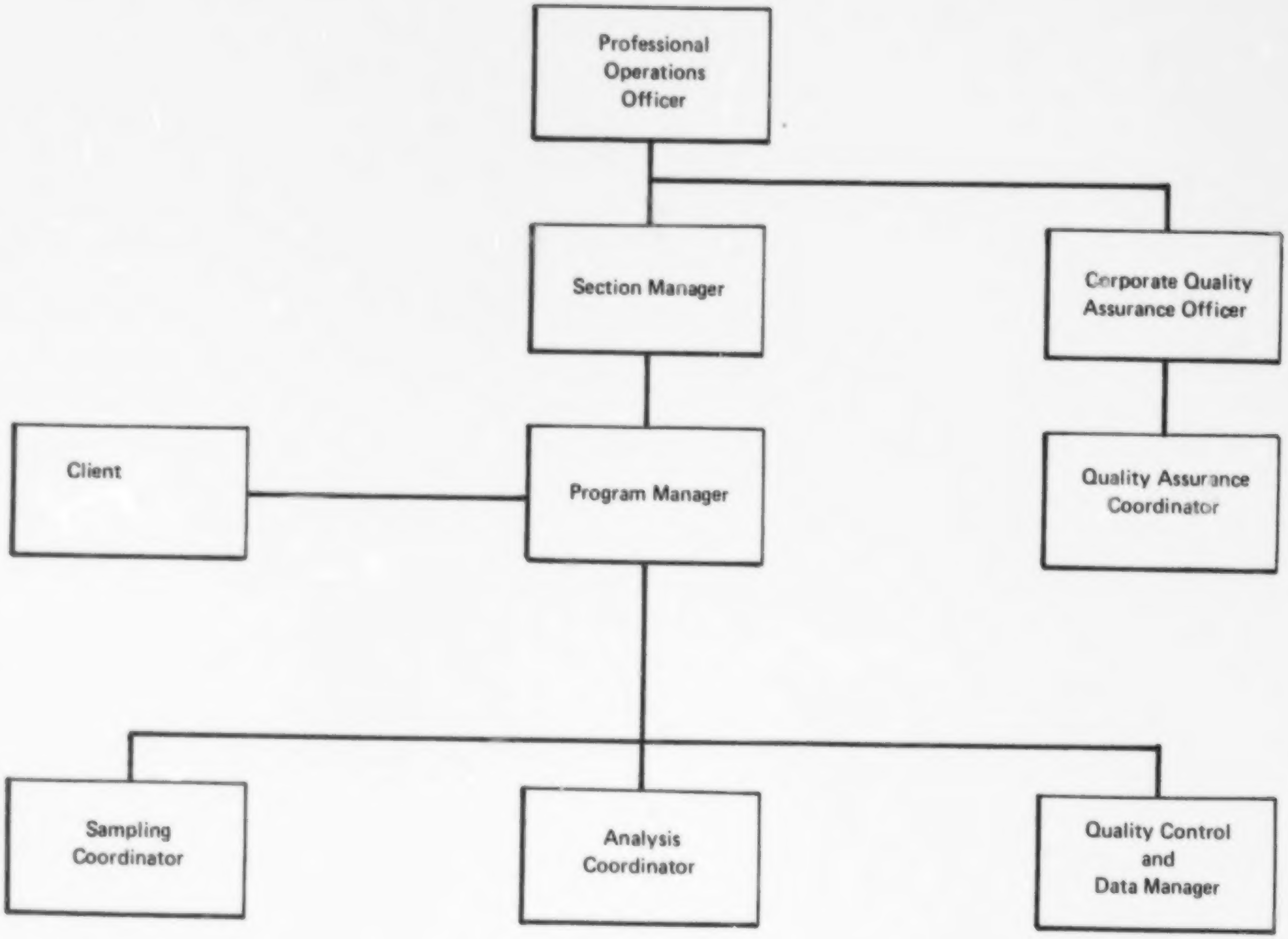
Professional
Operations
Officer
Section Manager
Corporate Quality
Assurance Officer
Client
Program Manager
Quality Assurance
Coordinator
Sampling
Coordinator
Analysis
Coordinator
Quality Control
and
Data Manager

FIGURE 9 EXAMPLE OF PROJECT ORGANIZATION AND RESPONSIBILITY

TABLE 16

SUMMARY OF ESTIMATED PRECISION, ACCURACY, AND COMPLETENESS OBJECTIVES[a]

Parameter	Precision[b]	Accuracy[b]	Completeness[c]
Flue gas dioxin/furans (Modified Method 5)	±	50-100	100
Ash dioxins/furans	±	50-100	100
Velocity/volumetric flow rate (EPA Method 1 & 2)	±	± 20	100
Fixed gases/molecular weight (Modified EPA Method 3)	± 10[f]	± 20[e]	100
Moisture (EPA Method 4)	± 20[d]	± 10[d]	100
Flue gas SO_2 (continuous monitor)	± 20[f]	± 20[e]	100
Flue gas temperature (thermocouple)	± 10°F	± 20°F	100
Ash (NAA)	ND	ND	100
Particulate Mass	± 10	± 12	100
Flue gas HCl (IC Analysis)	± 10	± 10	100
Flue Gas Lead/Cadmium (AA/AAF, NAA)	ND	ND	100
Flue Gas Chromium/Nickel (AA/AAF, NAA, Colorimetry)	± 10	± 10	100

[a] All objectives are expressed in terms of percent (%).

[b] Precision and accuracy estimated based on results of EPA collaborative tests.

[c] Valid data percentage of total tests conducted.

[d] Relative error (%) derived from audit analyses, where

$$\text{Percent} = \frac{\text{Measured Value - Actual Value}}{\text{Actual Value}} \times 100\%$$

[e] Coefficient of variation (CV) determined from daily analysis of a control sample where

$$\text{CV} = \frac{\text{Standard Deviation}}{\text{Mean}} \times 100\%$$

[f] Percent difference for duplicate analyses, where

$$\text{Percent} = \frac{\text{First Value - Second Value}}{0.5\ (\text{First + Second Values})} \times 100\%$$

ND - not determined for this method

Source: "Revised Sampling and Analytical Plan for the Marion County Solid Waste-to-Energy Facility Boiler Outlet Salem Oregon," EPA Contract No. 68-02-4338, DCN: 86-222-124-02-05, September 16, 1986.

- Specific sampling procedures to be used (by reference in the case of standard procedures and by actual description of the entire procedure in the case of nonstandard procedures).

- Charts, flow diagrams, or tables delineating sampling program operations.

- A description of containers, procedures, reagents, etc., used for sample collection, preservation, transport, and storage.

- Special conditions for the preparation of sampling equipment and containers to avoid sample contamination (e.g., containers for organics should be solvent-rinsed; containers for trace metals should be acid-rinsed).

- Sample preservation methods and holding times.

- Time considerations for shipping samples promptly to the laboratory.

- Sample preparation (e.g., concentration, dilution, cleanup techniques).

- Forms, notebooks, and procedures to be used to record sample history, sampling conditions, and analysis to be performed.

G. SAMPLE CUSTODY

It is essential that adequate chain-of-custody procedures be established for each project. The following sample custody procedures should be addressed in the QA Project Plans:

Field Sampling Operations:

- Documentation of procedures for preparation of reagents or supplies which become an integral part of the sample (e.g., filters and absorbing reagents).
- Procedures and forms for recording the exact location and specific consideration associated with sample acquisition.
- Documentation of specific sample preservation method.
- Pre-prepared sample labels containing all information necessary for effective sample tracking.
- Standardized field tracking reporting forms to establish sample custody in the field prior to shipment.

Laboratory Operations:

- Identification of the person responsible to act as sample custodian at the laboratory facility who is authorized to sign for incoming field samples, obtain documents of shipment (e.g., bill of lading number of mail receipt), and verify the data entered into the sample custody records.
- Provision for a laboratory sample custody log consisting of serially numbered standard lab-tracking report sheets.
- Specification of laboratory sample custody procedures for sample handling, storage, and dispersement for analysis.

H. CALIBRATION PROCEDURES AND FREQUENCY

For each critical measurement parameter, including all critical pollutant measurement systems, the following information should be included:

- Calibration procedures and information.

- Applicable standard operating procedure (SOP) or written description of the calibration procedure(s) to be used.

- Frequency planned for recalibration.

- Calibration standards to be used and their source(s), including traceability procedures and verification of purity procedures.

I. ANALYTICAL PROCEDURES

For each critical measurement parameter, the applicable standard operating procedure (SOP) should be referenced or a written description of the analytical procedure(s) to be used provided. Officially approved EPA procedures should be used when available and if applicable.

J. DATA REDUCTION, VALIDATION, AND REPORTING

For each critical measurement parameter, the following items should be briefly addressed:

- The data reduction scheme planned on collected data.

- All equations used to calculate the concentration or value of the measured parameter and the reporting units.

- The principal procedures that will be used to validate data integrity during collecting, transferring (if applicable), and reporting of data.

- The methods used to identify and treat outliers.

- The data flow or reporting scheme from collection of raw data through storage and validation of results. A flowchart will usually be needed.

- Key individuals who will handle the data in this reporting scheme. (If this has already been described under project organization and responsibilities, it need not be repeated here.)

K. INTERNAL QUALITY CONTROL CHECKS

This section presents guidelines for the number and frequency of replicate and spiked QC samples and calibration standards to be used, including concentration of surrogate or spike compounds to be added to designated QC samples. The QA plan should document the objectives for number, type, and frequency of QC samples.

Quality control samples are analyzed in the same way as field samples and interspersed with the field samples for analysis. The results of analyzing the QC samples are used to document the validity of data and to control the quality of data within predetermined tolerance limits. QC samples include blank samples, analytical replicates, and spiked samples.

Blank Samples

These samples are analyzed to assess possible contamination from the field and/or laboratory, so that corrective measures may be taken, if necessary. Blank samples include:

- Field Blanks--These blank samples are exposed to field and sampling conditions and analyzed to assess possible contamination from the field (a minimum of one for each type of sample to be collected and analyzed).

- Method Blanks--These blank samples are prepared in the laboratory and are analyzed to assess possible laboratory contamination (a minimum of one for each lot of samples analyzed).

- Reagent and Solvent Blanks--These blanks are prepared in the laboratory and analyzed to determine the background of each of the reagents or solvents used in an analysis (a minimum of one for each new lot number of solvent or reagent used).

Replicate Samples

These samples are analyzed in order to establish control and assess the precision of the analytical methodology. Replicate samples include:

- Field Replicates - These samples are collected in the field and analyzed in order to assess the reproducibility of the sampling program (a minimum of one for each sampling event per sample type and measurement parameter).

- Laboratory Replicates - These replicate samples are prepared in the laboratory in order to assess the reproducibility of the laboratory procedures used (a minimum of one for each lot of samples analyzed).

In addition, replicate analyses of specific samples may be undertaken by the analyst to check on the validity of any anomalous results. Such results could be the result of instrument or data system malfunction, operator error, laboratory contamination, etc. Repeat analyses of the sample in question and a previous "normal" sample will serve to indicate which of the possible problems is, in fact, present.

Spiked Samples

Samples may be spiked with one or more selected surrogate compounds prior to extraction and analysis. "Surrogate" compounds are defined as species that are chemically similar to the compounds being determined but that are not expected to be present in the samples (e.g., when GC/MS is the analytical method to be used, stable-isotope labelled analogs of the compounds sought are excellent surrogates). The data on surrogate concentrations are used to calculate surrogate compound recovery from each sample as one measure of the accuracy (bias) of the sample preparation and analysis procedures. To the extent that an analytical method (e.g., GC/MS) is consistent with use of surrogates, this procedure allows recovery to be estimated for every sample at trivial incremental cost to the testing. In some cases, e.g., trace metals, GC/ECD analyses, it may be difficult to select an appropriate surrogate compound that will mimic the behavior of the species sought but not lead to positive interferences in the analysis.

In addition to use of surrogate spiking (if possible), selected samples should be spiked with target analytes at a predetermined concentration level(s). This requires that each of the selected samples be carried through the entire sample preparation and analysis procedure twice, once unspiked and once spiked. Also, spiked blank samples for each measurement parameter should be analyzed in order to assess the inherent accuracy (bias) of the analytical method. To ensure that the per cent recovery of the spike can be determined with a reasonable degree of confidence, the spiking level should be at least 2-3 times the critical decision level (see Section II.A) and at least as high as the level expected in the unspiked sample. Depending on the concentration of analyte in the unspiked sample, these data may provide an estimate of the recovery of the species of interest from the sample matrix.For difficult sample matrices, multiple spiking levels may be used (method of standard additions).

L. PERFORMANCE AND SYSTEM AUDITS

Each QAPP should describe the internal performance evaluation and technical systems audits which are planned to monitor the capability and performance of the system(s) to be used for obtaining critical measurements.

The technical systems audit consists of an evaluation of all components of the critical measurement systems to determine their proper selection and use. This audit includes a careful evaluation of both field and laboratory quality control procedures. Systems audits are normally performed before or shortly after systems are operational; however, such audits should be performed on a regularly scheduled basis during the lifetime of the project of continuing operation. The on-site technical systems audit may be a requirement for formal laboratory certification programs.

After systems are operational and generating data, performance evaluation audits are conducted periodically, as appropriate, to determine the bias of the critical measurement system (s) or component parts thereof. The plan should include a schedule for conducting performance audits for each critical measurement parameter, including a performance audit for all measurement systems, should the nature of the work require that a performance audit be done. As part of the performance audit process, laboratories may be required to participate in the analysis of performance evaluation samples.

M. PREVENTIVE MAINTENANCE

The QA project plan for a trial burn should itemize the procedures for preventive maintenance that are relevant to the sampling analysis and efforts required in the project. For example, the following types of preventive maintenance items should be considered and addressed in the QA Project Plan:

- A schedule of important preventive maintenance tasks that must be carried out to minimize downtime of the critical measurement systems.

- A list of any critical spare parts that should be on hand to minimize downtime.

N. SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA PRECISION, ACCURACY, AND COMPLETENESS

The data quality indicators (e.g., precision, bias, completeness, and method detection limit (MDL)) should be routinely assessed for all critical measurement parameters. Specific procedures to assess precision, bias, completeness, and MDL on a routine basis should be described in each QA Project Plan, as applicable to the measurement parameter and the system being measured. The QA Project Plan should also contain and discuss any statistical or mathematical methods used to evaluate the measurement data.

O. CORRECTIVE ACTION

Corrective action procedures include the following elements and must be described for each project:

- The predetermined limits for data acceptability beyond which corrective action is required.
- Procedures for corrective action.
- For each critical measurement system, identify the individual responsible for initiating the corrective action and also the individual responsible for approving the corrective action, if necessary.

Corrective actions may also be initiated as a result of other QA activities, including:

- Performance evaluation audits.
- Technical systems audits.
- Laboratory/interfield comparison studies.

A formal corrective action program is difficult to define for these QA activities in advance and may be defined as the need arises.

If long-term corrective action is necessary to eliminate the cause of nonconformance, the following closed-loop corrective action system may be used. As appropriate, the sample coordinator, analysis coordinator or the program manager, ensures that each of these steps is followed:

1. The problem is defined.
2. Responsibility for investigating the problem is assigned.

3. The cause of the problem is investigated and determined.

4. A corrective action to eliminate the problem is determined.

5. Responsibility for implementing the corrective action is assigned and accepted.

6. The effectiveness of the corrective action is established and the correction implemented.

7. The fact that the corrective action has eliminated the problem is verified and documented.

P. QUALITY ASSURANCE REPORTS TO MANAGEMENT

QA Project Plans should provide a mechanism for periodic reporting to Management on the performance of critical measurement systems and data quality. As a minimum, these reports should include:

- Changes to the QA Project Plan, if any.
- Limitations or constraints on the use or applicability of the data, if any.
- Quality programs, quality accomplishments, and status of corrective actions.
- Results of QA systems and/or performance evaluation audits.
- Assessments of data quality in terms of precision, bias, completeness, representativeness, and comparability.
- Quality-related training.

The final report for each project must include a separate QA section that documents the QA/QC activities that lend support to the credence of the data and the validity of the conclusions.

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APPENDIX A

Equipment and Procedures Used in Milwaukee Sampling Program*

Overview

During the twelve-month period beginning August 3, 1959, one collection a week was made from each sample area. The material picked up included all garbage, ashes, combustible and noncombustible rubbish produced by the residents of the sample area.

A special City crew collected the material and separated it during collection into three categories: ashes, combustibles, and noncombustibles. Total weight, volume, density and moisture content determinations were made on each of the three categories. The percent that each component contributed to the total sample was then calculated. In addition to these physical tests, certain chemical analyses were made on the combustible and ash portions. The chemical tests included analyses for hydrogen, nitrogen, carbon, lipids, potassium, and phosphorus. Subsequent calculations for percent liquid content and C/N were also made. All tests were performed on each individual sample.

Equipment:

1. A dump truck was outfitted with a specially constructed bed to provide separate compartments for the ash, noncombustibles, and combustibles portions of the combined refuse. An Allis-Chalmers forage harvester (shredder) complete with necessary appurtenances including a loading platform, a 25 horsepower electric motor, a discharge spout, and all required safety devices was used.

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*Adapted from Reference 16.

2. Six 1 1/2 cubic yard steel bins complete with castors and a removable end.

3. A battery-operated fork lift.

4. A 1000 pound net-capacity platform scale rebuilt to provide an accuracy of 0.1 pounds.

6. Three 55 gallon drums.

7. A gram laboratory scale.

8. A forced air drying oven.

9. A Wiley Mill.

10. A sand splitter.

11. Eleven drying pans.

12. A hand tamp.

13. A Parr oxygen-bomb calorimeter.

14. Air-tight sample cans.

Sampling Procedure:

1. Collected refuse from appropriate sampling area. Separated material during collection into three separate components, ashes, noncombustibles, and combustibles.

2. Trucked material to central testing point. A corner of one of the cities incinerator buildings was used as this location.

3. Broke open the combustible packages and removed the unburnable items. All combustible material was placed in the proper movable bin and all non-combustibles were thrown into their respective truck compartment.

4. Processing of combustibles.

    a. All movable bins containing combustible refuse were weighed and volume measurements were taken prior to running the material through the shredder.

    b. The material was processed through the shredder four times. Two movable bins were placed under the discharge spout to halve the material each time it went through the machine. By halving the refuse four times the samples was reduced to one-sixteenth of its original size.

    c. The remaining material was quartered by a shovel, retaining about enough to fill a gallon container.

    d. Weight measurements were taken of all the combustible refuse prior to disposal to determine the moisture lost during the shredding operation.

    e. The sample was transferred from the gallon container to a drying pan and placed in the oven.

    f. Weight measurements pertinent to moisture content calculations were recorded.

    g. A sand splitter was used to quarter the sample after it was processed through a Wiley Mill where it was reduced to a maximum size of one millimeter. The size of the final quarter was about 100 grams.

    h. Fifty grams of this were sent for certain chemical analyses and the other 50 grams were returned to the drying oven. It was necessary to redry the material to eliminate moisture added during the grinding process.

i. The calorimeter test was performed and the information recorded.

5. Processing of Noncombustibles

   a. Noncombustibles were placed in the proper metal bins, weighed, and the volume determined.

   b. This material was stored in an empty bin and separated periodically into three separate components - cans, bottles. and miscellaneous noncombustibles. Data were recorded to enable calculation of the percent of total weight and volume represented by each component. The material was then thrown away.

   c. Once a week a grab sample was taken from the material produced by one classification. This sample was taken from a different area each week, thereby each area was tested once every 10 weeks.

   d. This sample was placed in a drying pan and then put into the oven.

   e. Weight measurements pertinent to moisture content calculations were recorded.

6. Processing of Ashes

   a. Ashes were placed in the proper bin, weighed and volume measurements were taken.

   b. The ashes were quartered by shovel, retaining approximately a pint of material.

   c. The pint sample was placed in an air-tight container and stored until all such ash samples for the week were placed therein.

d. At the end of the week the sample container was emptied and the lumps were reduced with a hand tamp.

e. The material was quartered with the sand splitter, retaining about 2 pounds.

f. A moisture content was made by use of the drying oven and the pertinent weight measurements were recorded.

g. The dried ash was reduced to a weight of about 400 grams with the sand splitter.

h. Half of this was sent to Purdue for further analyses and half was returned to the drying oven.

i. After a second drying period, a calorimeter test was performed.

APPENDIX B

ASME-EPA DRAFT ENVIRONMENTAL STANDARDS PROTOCOLS FOR SAMPLING AND ANALYSIS OF PCDD/PCDF IN MSW COMBUSTOR EFFLUENTS

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STANDARD PROTOCOL FOR RECORDING
FURNACE OPERATING DATA DURING SAMPLING FOR
TRACE EMISSIONS OF CHLORINATED ORGANIC COMPOUNDS
IN ENERGY FROM SOLID WASTE COMBUSTION PLANTS

TRODUCTION

The information on furnace operation which should be gathered during
ts for trace emissions of chlorinated organic compounds is summarized in
following data form. It will be noted that actual values while sampling
underway in the form of copies of actual strip charts is the preferable
rm of reporting operating information.

Where design information is requested, it should be characteristic of
mal operation at the time of year when sampling is actually being done.
parison between the expected and actual values during sampling is a guide
to whether the system was operating normally while it was being sampled.
the comparison suggests the system may not have been operating normally
ring sampling, it may be difficult to utilized the data.

It will also be noted that some of the required information is to be
llected as nearly continuously as possible during sampling. This is so as
permit detection of changes, intended and inadvertent, which may have
curred during sampling. The occurrence or absence of any such changes is a
ctor in interpreting the results of the sampling.

Recording the essential information shall begin at least three hours
fore sampling is begun and be continued for at least an hour after sampling
terminated.

The following form is intended to accompany reports on source sampling
refuse-to-energy facilities.

ACKGROUND INFORMATION

1. Name and address of the facility: ______________________________
____
____

2. Name and telephone number of plant general manager or other person to contact regarding emission sampling program:
______________________________ # ______________________________

3. Name and telephone number of emission sampling team manager:
______________________________ # ______________________________

4. Name and telephone number of person responsible for laboratory analysis of samples:
______________________________ # ______________________________

5. Name and telephone number of meteorological monitoring station servicing the locality of the plant:
______________________________ # ______________________________

6. Designation of the combustion train actually sampled:
______________________________ # ______________________________

7. Date of emission sampling: ______________________________
Time when sampling started: ______________________________
Time when sampling terminated: ______________________________

FACILITY DESCRIPTION

8. Type of refuse processing system (e.g., mass-burn, refuse derived fuel):
____

9. Describe refuse preparation method, if appropriate: ______________________________
____

10. Type of furnace (e.g., waterwall, refractory-wall, hybrid): ______________________________
____
Is auxiliary fuel regularly fired? If so, what fuel? ______________________________

11. Design heat release rate (MMBtu/hr): ______________________________

12. Design steam production rate and conditions: ______________ lbs/hr @
______________ °F, ______________ psig, and (if saturated) ______________ % quality.

13. Feed properties for which unit was designed:
- Range of heating values ______________ to ______________ Btu/lb
- Range of moisture contents ______________ to ______________ wt %
- Range of ash contents ______________ to ______________ wt %

14. Please provide a cross-sectional diagram of the facility, preferably to scale, showing the spatial relationship between the major elements of the process train, including: the waste feed system to the grate; the grate

and residue removal system; shape of the furnace; primary and secondary combustion air ports; the boiler and its flue gas passages; soot blowers; major heat transfer surfaces; economizer; air preheater (if appropriate); air pollution control system; induced draft fan; and stack. Indicate locations of temperature and pressure detectors also.

5. Description of the grate system:

- Supplier: ______________________
- Type (e.g., reciprocating, roller, traveling, rotary): __________
- Number of step sections (if appropriate): __________
- Grate area (ft^2) (or equivalent): __________

6. Description of the boiler:

- Supplier: ______________________
- Furnace volume (ft^3): ______________________
- Firebox dimensions (ft): L __________ W __________ H __________
- Kind of soot blowers: ______________________
- Soot blowing schedule (approximate times): __________

17. Type of combustion (e.g., excess air, starved air): __________

____

18. Overfire and underfire air distribution:

- Describe design and type of all air ports: __________

  ____

  ____

- Describe how total combustion air and air distribution is controlled

  ____

  ____

- Verify that air distribution systems are operating as designed:

  ____

  ____

19. Type of draft: ______________________

How is draft regulated: ______________________

20. Description of solid waste feeding and stoking system:

- How is feeding rate controlled? __________
- Frequency and length of feed ram stroke: __________

21. Describe the overall plant control system logic (e.g., what measurements are used as the basis for controlling firing rate?): __________

____

22. Stack height (ft): ______________________

Stack diameter at top (ft): ______________________

23. Type of air pollution control system: __________

24. If electrostatic precipitator:

- Specific collection area (ft^2/1000 ACFM): __________
- Design temperature at inlet (°F): __________
- Number of independent bus sections: __________
- Which independent bus sections were in service during emission sampling? __________
- Design particulate loading at inlet: __________ grains/dscf

  at outlet: __________ grains/dscf

Rapping frequency: ______________________

25. If fabric filter:

- Fabric type __________ Weight __________ Weave __________ Finish __________
- Bag cleaning method and frequency: __________

  ____

- Air-to-cloth ratio (ACFM/ft^2): __________
- Design pressure drop across bags (in., W.C.): __________
- Design gas temperature at inlet (°F): __________
- Total number of bags: ______________________

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- Actual number of bags in service at time of sampling: ____________
- Range in pressure drop across bags during testing: ____________

. Which flue gas components are regularly measured? Indicate location of monitor:

	Instrument Model	Location	Unit Served by This Monitor
Oxygen			
Carbon Monoxide			
Hydrocarbons			
Other (Specify)			

Is flue gas opacity regularly monitored? ____________

. Description of existing temperature monitors:

Locations: ____________

Type of temperature detector(s): ____________

Manufacturer and model number: ____________

Date of most recent calibration: ____________

1. Time constants of in-plant measuring devices (pressure gauges, flue gas monitors, thermocouples): ____________

). What is the voluntary shutdown schedule for routine maintenance of the process train being sampled? ____________

Dates of the most recent shutdown for routine maintenance and type of maintenance performed? ____________

0. Types of refuse normally accepted at the facility (please indicate source of this information):

	Approximate Percentage
Residential	
Commercial/Institutional	
Industrial	
Construction debris	
Known hazardous waste	

TEST DATA

31. Barometric pressure at start of test (in. Hg): ____________

32. Precipitation over seven days prior to test (in.) by day: ____________

33. Relative humidity at start of test: ____________

34. Temperature of combustion air after any air heaters (°F):

    Underfire ____________ Overfire ____________

35. Temperatures of combustion air at inlets to forced draft fan (°F):

    Underfire ____________ Overfire ____________

36. Combustion air flow rates (ACFM preferable) or pressure if flow is not available - include strip chart record if available or record measurements on indicators at 15 minute intervals at a minimum:

    Underfire ____________ Overfire ____________

37. Solid waste firing rate over test period (attach strip chart record if available; if not available, give total quantity of waste fired over sampling period and maximum and minimum firing rates): ____________

    Indicate method of determining firing rate [load cell, crane count, ram cycle, other (specify)]: ____________

38. Auxiliary fuel firing rate over test period (attach strip chart record if available; if not available, give total quantity of waste fired over sampling period and maximum and minimum firing rates): ____________

39. If soot blowing occurs during sampling period, give times and duration: ____________

40. Furnace temperatures:

    - Design temperatures and locations: _____°F, ____________
    - Attach summary record of furnace temperature measurements during corresponding month of past years

- Attach strip chart record of temperature at top of furnace, in front of screen tubes - over the sampling period (if records are available for more than one in-plant thermocouple, include them and specify their locations)

41. Flue gas analysis:

    - Attach strip chart records for concentrations of the following flue gas constituents, measured over the sampling period: carbon monoxide, carbon dioxide, oxygen, nitrogen oxide, sulfur dioxide, total hydrocarbons, water vapor, and flue gas flow

    - Attach strip chart record for in-stack opacity over the sampling

42. Include a copy of the operator's log for the period of the test.

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SAMPLING FOR THE DETERMINATION OF CHLORINATED ORGANIC COMPOUNDS IN STACK EMISSIONS

PRINCIPLE AND APPLICABILITY

1.1 **Principle:** Stack gases that may contain chlorinated organic compounds are withdrawn from the stack using a sampling train. The analyte is collected in the sampling train. The compounds of interest are determined by solvent extraction followed by gas chromatography/mass spectroscopy (GC/MS).

1.2 **Applicability:** This method is applicable for the determination of chlorinated organic compounds in stack emissions. The sampling train is so designed that only the total amount of each chlorinated organic compound in the stack emissions may be determined. To date, no studies have been performed to demonstrate that the particulate and/or gaseous chlorinated organic compounds collected in separate parts of the sampling train accurately describes the actual partition of each in the stack emissions. If separate parts of the sampling train are analyzed separately, the data should be included and so noted as in Section 2 below. The sampling shall be conducted by competent personnel experienced with this test procedure and cognizant of intricacies of the operation of the prescribed sampling train and constraints of the analytical techniques for chlorinated organic compounds, especially PCDDs and PCDFs.

Note: This method assumes that all of the compounds of interest are collected either on the XAD-2 resin or in upstream sampling train components. Since the method at the present time has not been validated in the presence of all the other components present (HCl, high organic load) in the stack emission, it is recommended that appropriate quality control (QC) steps be employed until such validation has been completed. These QC steps may include the use of a backup resin trap or the addition of a representative labeled standard (distinguishable from the internal standard used for quantitation) to the filter and/or the XAD-2 in the field prior to the start of sampling. These steps will provide information on possible breakthrough of the compounds of interest.

2. REPORTABILITY

Recognizing that modification of the method may be required for specific applications, the final report of a test where changes are made shall include: (1) the exact modification; (2) the rationale for the modification; and (3) an estimate of the effect the modification will produce on the data.

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3. RANGE OF MINIMUM DETECTABLE STACK GAS CONCENTRATION

The range of the analytical method may be expanded considerably through concentration and/or dilution. The total method sensitivity is also highly dependent on the volume of stack gas sampled and the detection limit of the analytical finish. The user shall determine for their system the minimum detectable stack gas concentration for the chlorinated organic compounds of interest. The minimum detectable stack gas concentration should generally be in the ng/m^3 (nanogram/cubic meter) or lower range.

4. INTERFERENCES

Organic compounds other than the compounds of interest may interfere with the analysis. Appropriate sample clean-up steps shall be performed. Through all stages of sample handling and analysis, care should be taken to avoid contact of samples and extracts with synthetic organic materials other than polytetrafluorethylene (TFE®). Adhesives should not be used to hold TFE® liners on lids (but, if necessary, appropriate blanks must be run), and lubricating and sealing greases must not be used on the sampling train.

5. PRECISION AND ACCURACY

Precision and accuracy measurements have not yet been made on PCDD and PCDF using this method. These measurements are needed. However, recovery efficiencies for source samples spiked with compounds have ranged from 70 to 120%.[1,3]

6. SAMPLING RUNS, TIME, AND VOLUME

6.1 **Sampling Runs:** The number of sampling runs must be sufficient to provide minimal statistical data and in no case shall be less than three (3).

6.2 **Sampling Time:** The sampling time must be of sufficient length to provide coverage of the average operating conditions of the source. However, this shall not be less than three hours (3).

6.3 **Sample Volume:** The sampling volume must be sufficient to provide the required amount of analyte to meet both the MDL of the analytical finish and the allowable stack emissions. It may be calculated using the following formula:

$$\text{Sample Volume} = A \times \frac{100}{B} \times \frac{100}{C} \times \frac{1}{D}$$

A = The analytical MDL in ng
B = Percent (%) of the sample required per analytical finish run

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C = The sample recovery (%)
D = The allowable stack emissions (ng/m^3)

Example: A = 0.050 ng; B = 10%; C = 50%; and D = 1 ng/m^3

$$SV = 0.05 \times \frac{100}{10} \times \frac{100}{50} \times \frac{1}{1} = 1m^3$$

7. APPARATUS

Sampling Train: The train consists of nozzle, probe, heated particulate filter, and sorbent module followed by four impingers (Fig. 1). Provision is made for the addition of (1) a cyclone in the heated filter box when testing sources emitting high concentrations of particulate matter, (2) a large water trap between the heated filter and the sorbent module for stack gases with high moisture content, and (3) additional impingers following the sorbent module. If one of the options is utilized, the option used shall be detailed in the report. The train may be constructed by adaption of an EPA Method 5 train. Descriptions of the sampling train components are contained in the following sections.

7.1.1 Nozzle

The nozzle shall be made to the specifications of EPA Method 5. The nozzle may be made of nickel plated stainless steel, quartz, or borosilicate glass.

7.1.2 Probe

The probe shall be lined or made of TFE®, borosilicate, or quartz glass. The liner or probe extends past the retaining nut into the stack. A temperature controlled jacket provides protection of the liner or probe. The liner or probe shall be equipped with a connecting fitting that is capable of forming a leak-free, vacuum-tight connection without sealing greases.

7.1.3 Sample Transfer Lines (optional)

The sample transfer lines, if needed, shall be heat traced, heavy walled TFE® (1.3 cm [1/2 in.] O.D. x 0.3 cm [1/8 in.] wall) with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases. The line should be as short as possible and must be maintained at 120°C.

7.1.4 Filter Holder

Borosilicate glass, with a glass frit filter support and a glass-to-glass seal or TFE® gasket. A rubber gasket shall not be used. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe (or cyclone, if used).

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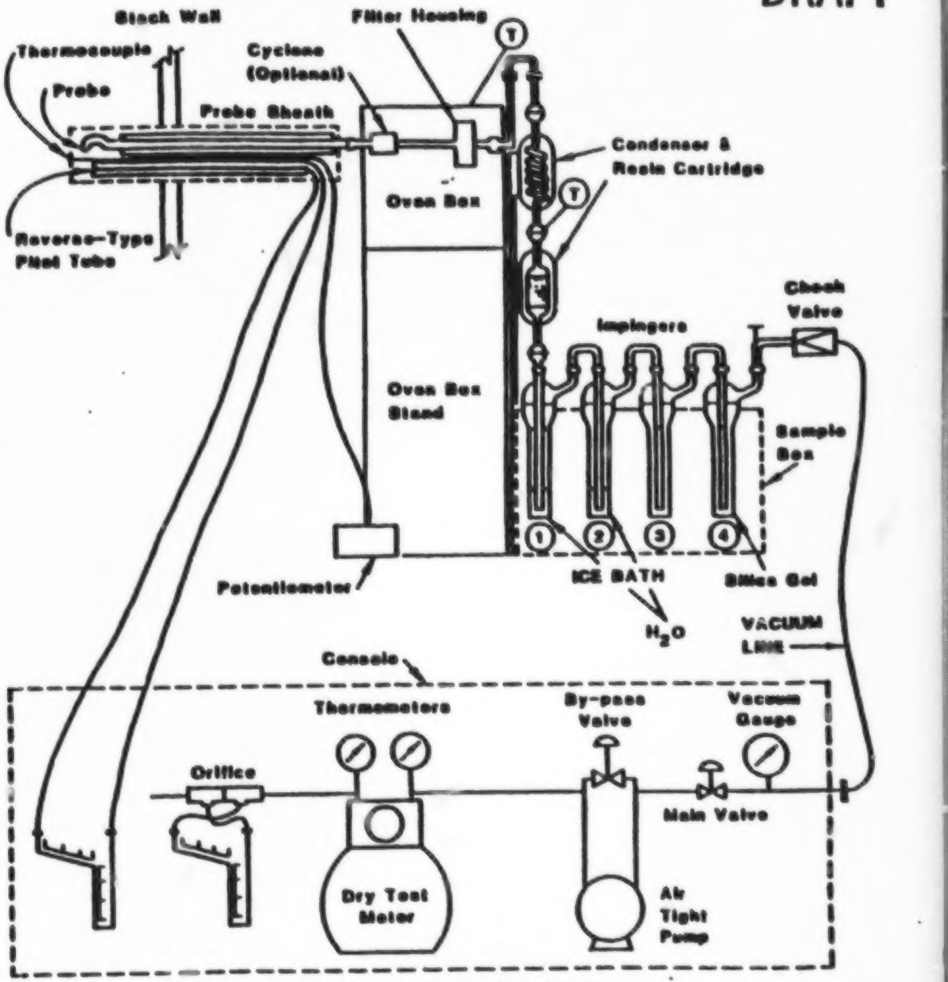
Stack Wall
Filter Housing
Thermocouple
Probe
Cyclone (Optional)
Probe Sheath
T
Condenser & Resin Cartridge
Oven Box
Reverse-Type Pitot Tube
Check Valve
Impingers
Oven Box Stand
Sample Box
1
2
3
4
Potentiometer
ICE BATH
Silica Gel
H$_2$O
VACUUM LINE
Console
Thermometers
By-pass Valve
Vacuum Gauge
Orifice
Main Valve
Dry Test Meter
Air Tight Pump

Impingers are of the Modified Greenberg-Smith Type
Impingers 1 and 2 Contain 100 ml Water
Impinger 3 Empty
Impinger 4 Contains 200-300 Grams Silica Gel
Impinger 1 is the Hexane-Rinsed Back-Up to the Resin Cartridge
(T) = Thermocouple location

Fig. 1. Modified EPA Method 5 Train for Organics Sampling

Source: Methods Manual Sampling and Analysis Procedures for Assessing Organics Emiss from Stationary Combustion Sources in Exposure Evaluation Division Studies, U.S. Environmental Protection Agency Report No. EPA-560-82-014 (January 1982)

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7.1.5 Cyclone in Filter Box (optional)

The cyclone shall be constructed of borosilicate glass with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases.

7.1.6 Filter Heating System

The heating system must be capable of maintaining a temperature around the filter holder (and cyclone, if used) during sampling of 120±14°C (248±25°F). A temperature gauge capable of measuring temperature to within 3°C (5.4°F) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling.

7.1.7 Solid Sorbent Module

Amberlite XAD-2® resin (XAD-2), confined in a trap, shall be used as the sorbent. The sorbent module shall be made of glass with connecting fittings that are able to form leak-free, vacuum-tight seals without use of sealant greases (Figs. 2 and 3). The XAD-2 trap must be in a vertical position. It is preceded by a coil-type condenser, also oriented vertically, with circulating cold water. Gas entering the sorbent module must be maintained at ≤20°C (68°F). Gas temperature shall be monitored by a thermocouple placed either at the inlet or exit of the sorbent trap. The sorbent bed must be firmly packed and secured in place to prevent settling or channeling during sample collection. Ground glass caps (or equivalent) must be provided to seal the sorbent-filled trap both prior to and following sampling. All sorbent modules must be maintained in the vertical position during sampling.

7.1.8 Impingers

Four or more impingers with connecting fittings able to form leak-free, vacuum-tight seals without sealant greases when connected together, shall be used. All impingers are of the Greenburg-Smith design modified by replacing the tip with 1.3 cm (1/2 in.) ID glass tube extending to 1.3 cm (1/2 in.) from the bottom of the flask.

7.1.9 Metering System

The metering system shall consist of a vacuum gauge, a leak-free pump, thermometers capable of measuring temperature to within 3°C (~5°F), a dry gas meter with 2 percent accuracy at the required sampling rate, and related equipment, or equivalent.

7.1.10 Barometer

Mercury, aneroid, or other barometers capable of measuring atmospheric pressure to within 2.5 Hg (0.1 in. Hg) shall be used.

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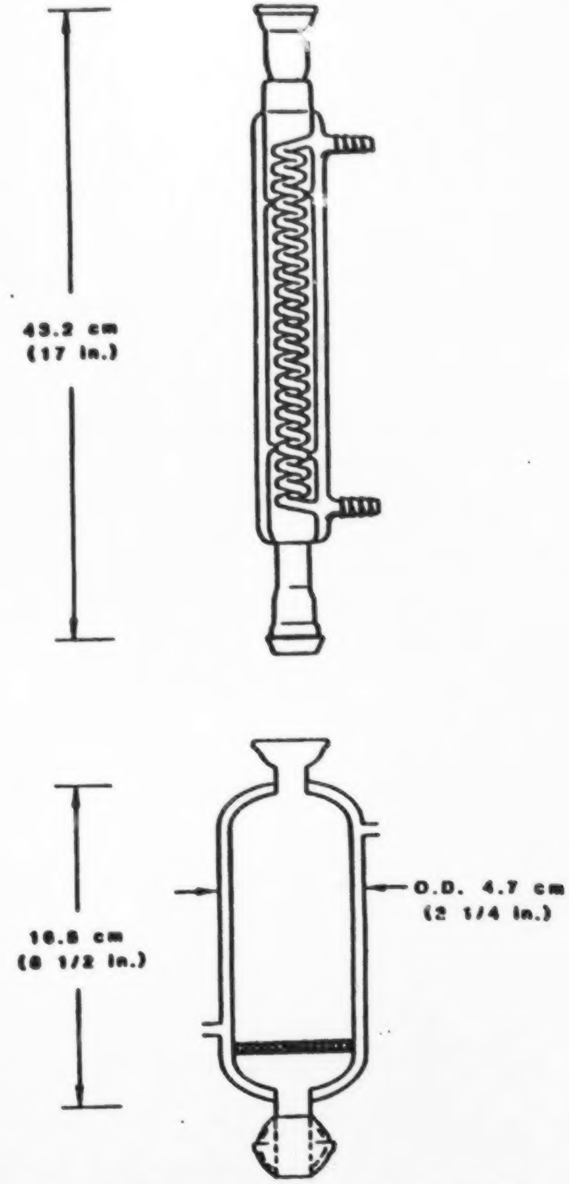

Fig. 2 Acceptable Sorbent Module Design #1

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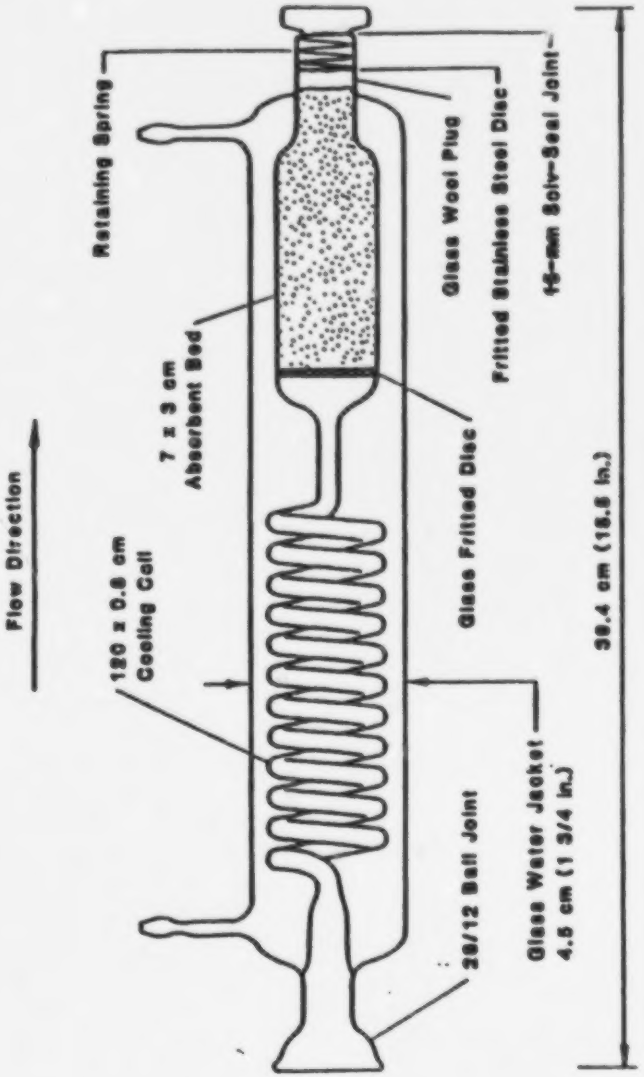
Flow Direction
Retaining Spring
7 x 3 cm
Absorbent Bed
120 x 0.8 cm
Cooling Coil
Glass Wool Plug
Fritted Stainless Steel Disc
15-mm Solv-Seal Joint
Glass Fritted Disc
Glass Water Jacket
4.5 cm (1 3/4 in.)
28/12 Ball Joint
38.4 cm (15.5 in.)

Fig. 3 Acceptable Sorbent Module Design #2

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7.2 Sample Recovery, Supplies, and Equipment

7.2.1 Ground Glass Caps or Hexane Rinsed Aluminum Foil

To cap off adsorbent tube and the other sample-exposed portions of the train. If TFE® screw connections are used, then TFE® screw caps shall be used.

7.2.2 Teflon FEP® Wash Bottle

Three 500 ml, Nalgene No. 0023A59, or equivalent.

7.2.3 Probe and Transfer Line Brush

Inert bristle brush with stainless steel rod-handle of sufficient length that is compatible with the liner or probe and transfer line.

7.2.4 Filter Storage Containers

Sealed filter holder or precleaned, wide-mouth amber glass containers with TFE®-lined screw caps or wrapped in hexane rinsed aluminum foil.

7.2.5 Balance

Triple beam, Ohaus model 7505, or equivalent.

7.2.6 Aluminum Foil

Heavy duty, hexane-rinsed.

7.2.7 Precleaned Metal Can

To recover used silica gel.

7.2.8 Precleaned Graduated Cylinder, e.g., 250 ml

250 ml, with 2 ml graduations, borosilicate glass.

7.2.9 Liquid Sample Storage Containers

Precleaned amber glass bottles or clear glass bottles wrappe in opaque material, 1 L, with TFE®-lined screw caps.

8. REAGENTS

8.1 Sampling

8.1.1 Filter -- Fiberglass Reeve-Angel 934 AH or Equivalent

Prior to use in the field, each lot of filters shall be subjected to precleaning and a quality control (QC) contamination check to confirm that there are no contaminants present that wil

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nterfere with the analysis of analyte at the target detection imits.

If performed, filter precleaning shall consist of Soxhlet xtraction, in batches not to exceed 50 filters, with the solent(s) to be applied to the field samples. As a QC check, the xtracting solvent(s) shall be subjected to the same concentraion, cleanup and analysis procedures to be used for the field amples. The background or blank value observed shall be conerted to a per filter basis and shall be corrected for any ifferences in concentration factor between the QC check (CF_{QC}) nd the actual sample analysis procedure (CF_s).

$$\text{Blank value per filter} = \frac{\underline{\text{Apparent } \mu g \text{ of analyte}}}{\text{No. filters extracted}} \times \frac{CF_s}{CF_{QC}}$$

where:

$$CF = \frac{\underline{\text{Initial volume of extracting solvent}}}{\text{Final Volume of concentrated extract}}$$

The quantitative criterion for acceptable filter quality will depend on the detection limit criteria established for the field sampling and analysis program. Filters that give a background or blank signal per filter greater than or equal to the target detection limit for the analyte(s) of concern shall be rejected for field use. Note that acceptance criteria for filter cleanliness depends not only on the inherent detection limit of the analysis method but also on the expected field sample volume and on the desired limit of detection in the sampled stream.

If the filters do not pass the QC check, they shall be re-extracted and the solvent extracts re-analyzed until an acceptably low background level is achieved.

8.1.2 Amberlite XAD-2 Resin

The cleanup procedure may be carried out in a giant Soxhlet extractor, which will contain enough Amberlite XAD-2® resin (XAD-2) for several sampling traps. An all glass thimble 55-90 mm OD x 150 mm deep (top to frit) containing an extra coarse frit is used for extraction of XAD-2. The frit is recessed 10-15 mm above a crenelated ring at the bottom of the thimble to facilitate drainage. The XAD-2 must be carefully retained in the extractor cup with a glass wool plug and stainless steel screen since it floats on methylene chloride. This process involves sequential extraction in the following order.

Solvent	Procedure
Water	Initial rinse with 1 L H_2O for 1 cycle, then discard H_2O
Water	Extract with H_2O for 8 hr
Methyl alcohol	Extract for 22 hr
Methylene chloride	Extract for 22 hr
Hexane	Extract for 22 hr

The XAD-2 must be dried by one of the following techniques.

(a) After evaluation of several methods of removing residual solvent, a fluidized-bed technique has proven to be the fastest and most reliable drying method.

A simple column with suitable retainers as shown in Fig. 4 will serve as a satisfactory column. A 10.2 cm (4 in.) diameter Pyrex pipe 0.6 m (2 ft. long) will hold all of the XAD-2 from the Soxhlet extractor, with sufficient space for fluidizing the bed while generating a minimum XAD-2 load at the exit of the column.

The gas used to remove the solvent is the key to preserving the cleanliness of the XAD-2. Liquid nitrogen from a regular commercial liquid nitrogen cylinder has routinely proven to be a reliable source of large volumes of gas free from organic contaminants. The liquid nitrogen cylinder is connected to the column by a length of precleaned 0.95 cm (3/8 in.) copper tubing, coiled to pass through a heat source. As nitrogen is bled from the cylinder, it is vaporized in the heat source and passes through the column. A convenient heat source is a water bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40°C. Experience has shown that about 500 g of XAD-2 may be dried overnight consuming a full 160 L cylinder of liquid nitrogen.

As a second choice, high purity tank nitrogen may be used to dry the XAD-2. The high purity nitrogen must first be passed through a bed of activated charcoal approximately 150 mL in volume. With either type of drying method, the rate of flow should gently agitate the bed. Excessive fluidation may cause the particles to break up.

(b) As an alternate, if the nitrogen process is not available, the XAD-2 may be dried in a vacuum oven, if the temperature never exceeds 20°C.

The XAD-2, even if purchased clean, must be checked for both methylene chloride and hexane residues, plus normal blanks before use.

(c) Storage of Clean XAD-2: XAD-2 cleaned and dried as prescribed above is suitable for immediate use in the field, provided it passes the QC contamination check described in (d), below. However, precleaned dry XAD-2 may develop unacceptable levels of contamination if stored for periods exceeding a few weeks.

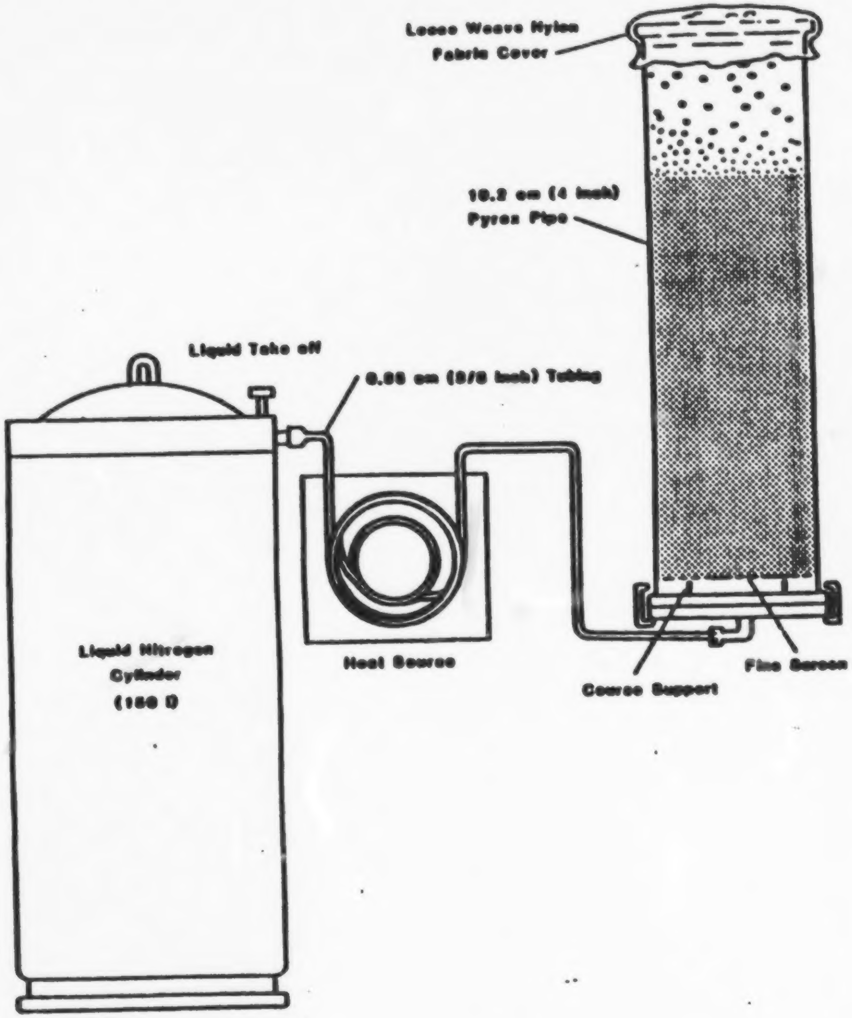
Loose Weave Nylon Fabric Cover
10.2 cm (4 inch) Pyrex Pipe
Liquid Take off
0.95 cm (3/8 inch) Tubing
Liquid Nitrogen Cylinder (160 l)
Heat Source
Coarse Support
Fine Screen

Fig. 4 XAD-2 Fluidized-Bed Drying Apparatus

If precleaned XAD-2 is not to be used immediately, it shall be stored under distilled-in-glass methanol. No more than two weeks prior to initiation of field sampling, the excess methanol shall be decanted; the XAD-2 shall be washed with a small volume of methylene chloride and dried with clean nitrogen as described in (b) above. An aliquot shall then be taken for the QC contamination check described in (d), below.

If the stored XAD-2 fails the QC check, it may be recleaned by repeating the final two steps of the extraction sequence above: sequential methylene chloride and hexane extraction. The QC contamination check shall be repeated after the XAD-2 is recleaned and dried.

(d) QC Contamination Check: The XAD-2, whether purchased, "precleaned", or cleaned as described above, shall be subjected to a QC check to confirm the absence of any contaminants that might cause interferences in the subsequent analysis of field samples. An aliquot of XAD-2, equivalent in size to one field sampling tube charge, shall be taken to characterize a single batch of XAD-2.

The XAD-2 aliquot shall be subjected to the same extraction, concentration, cleanup, and analytical procedure(s) as is (are) to be applied to the field samples. The quantitative criteria for acceptable XAD-2 quality will depend on the detection limit criteria established for the field sampling and analysis program. XAD-2 which yields a background or blank signal greater than or equal to that corresponding to one-half the MDL for the analyte(s) of concern shall be rejected for field use. Note that the acceptance limit for XAD-2 cleanliness depends not only on the inherent detection limit of the analytical method but also on the expected field sample volume and on the desired limit of detection in the sampled stream.

8.1.3 Glass Wool

Cleaned by thorough rinsing, i.e., sequential immersion in three aliquots of hexane, dried in a 110°C oven, and stored in a hexane-washed glass jar with TFE®-lined screw cap.

8.1.4 Water

Deionized, then glass-distilled, and stored in hexane-rinsed glass containers with TFE®-lined screw caps.

8.1.5 Silica Gel

Indicating type, 6-16 mesh. If previously used, dry at 175±5C for 2 hr. New silica gel may be used as received.

8.1.6 Crushed Ice

Place crushed ice in the water bath around the impingers during sampling.

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SAMPLE RECOVERY REAGENTS

1 Acetone

Pesticide quality, Burdick and Jackson "Distilled in Glass" or uivalent, stored in original containers. A blank must be reened by the analytical detection method.

2 Hexane

Pesticide quality, Burdick and Jackson "Distilled in Glass" or uivalent, stored in original containers. A blank must be reened by the analytical detection method.

). PROCEDURE

Caution: Sections 10.1.1.2 and 10.1.1.3 shall be done in the laboratory.

0.1 Sampling

0.1.1 Pretest Preparation

All train components shall be maintained and calibrated ccording to the procedure described in APTD-0576 unless otherwise pecified herein.

Weigh several 200 to 300 g portions of silica gel in air-tight ontainers to the nearest 0.5 g. Record the total weight of the ilica gel plus container, on each container. As an alternative, he silica gel may be weighed directly in its impinger or sampling older just prior to train assembly.

Check filters visually against light for irregularities and laws or pinhole leaks. Pack the filters flat in a precleaned lass container or wrapped hexane-rinsed aluminum foil.

10.1.1.1 Preliminary Determinations

Select the sampling site and the minimum number of sampling points according to EPA Method 1. Determine the stack pressure, temperature, and the range of velocity heads using EPA Method 2; it is recommended that a leak-check of the pitot lines (see EPA Method 2, Sec. 3.1) be performed. Determine the moisture content using EPA Approximation Method 4 or its alternatives for the purpose of making isokinetic sampling rate-settings. Determine the stack gas dry molecular weight, as described in EPA Method 2, Sec. 3.6; if integrated EPA Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the EPA Method 4 sampling.

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Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of EPA Method 2).

Select a suitable probe length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probes.

Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that (1) the sampling time per point is not less than 2 min., and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume determined in Section 6.3. The latter is based on an approximate average sampling rate.

It is recommended that the number of minutes sampled at each point be an integer or an integer plus one-half minute, in order to avoid time-keeping errors.

10.1.1.2 Cleaning Glassware

All glass parts of the train upstream of and including the sorbent module and the first impinger should be cleaned as described in Section 3A of the 1980 issue of "Manual of Analytical Methods for the Analysis of Pesticides in Humans and Environmental Samples."[3] Special care should be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. These grease residues should be removed by soaking several hours in a chromic acid cleaning solution prior to routine cleaning as described above.

10.1.1.3 Amberlite XAD-2 Resin Trap

Use a sufficient amount (at least 30 gms or 5 gms/m^3 of stack gas to be sampled) of cleaned XAD-2 to fill completely the glass sorbent trap which has been thoroughly cleaned as prescribed and rinsed with hexane. Follow the XAD-2 with hexane-rinsed glass wool and cap both ends. These caps should not be removed until the trap is fitted into the train. See Fig. 1 for details.

The dimensions and XAD-2 capacity of the sorbent trap, and the volume of gas to be sampled, should be varied as necessary to ensure efficient collection of the species of interest. Some illustrative data are presented in Table 1.

10.1.2 Preparation of Collection Train

During preparation and assembly of the sampling train, keep all train openings where contamination can enter covered until

TABLE 1

SAMPLE SIZE AND FLOW RATE COMPARISON FOR SEVERAL SORBENT TRAP DESIGNS

Trap	Dimensions (mm)		Charge of XAD-2 Resin (g)	Flow Equivalent to 43 cm/sec ^{a}	Max. Sample Size (cm^3) for Efficient Capture of Following Compounds^b		
	Depth	Diameter			Octane	Benzene	Phenol
SASS	70	90	130	165 Lpm (5.9 cfm)	130	3.0	240
ADL	70	45	40	40 Lpm (1.5 cfm)	45	0.9	74
Battelle	70	30	19	18 Lpm (0.65 cfm)	22	0.4	35

^{a}Upper limit beyond which collection efficiency drops off.

^{b}Calculated from V_g^T for 50% breakthrough. Specified value includes a safety factor of 2.

just prior to assembly or until sampling is about to begin. Caution: Do not use sealant greases in assembling the train.

Place approximately 100 gms of water in each of the first two impingers with a graduated cylinder, and leave the third impinger empty. Place approximately 200 to 300 g or more, if necessary, of silica gel in the last impinger. Weigh each impinger (stem included) and record the weights on the impingers and on the data sheet.

Assemble the train as shown in Fig. 1.

Place crushed ice in the water bath around the impingers.

10.1.3 Leak Check Procedures

10.1.3.1 Initial Leak Check

The train, including the probe, will be leak checked prior to being inserted into the stack after the sampling train has been assembled. Turn on and set (if applicable) the heating/cooling system(s) to cool the sample gas yet remain at a temperature sufficient to avoid condensation in the probe and connecting line to the first impinger (approximately 120°C). Allow time for the temperature to stabilize. Leak check the train at the sampling site by plugging the nozzle with a TFE® plug and pulling a 380 mm Hg (12 in. Hg) vacuum. A leakage rate in excess of 4% of the average sampling rate or 0.0057 m^3/min (0.02 cfm) whichever is less, is unacceptable. Sampling must cease if pressure during sampling exceeds the leak check pressure.

The following leak check instruction for the sampling train described in APTD-0576[2] and APTD-0581[4] may be helpful. Start the pump with bypass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the bypass valve until 380 mm Hg (12 in. Hg) vacuum is reached. Do not reverse the direction of the bypass valve. This will cause water to back up into the probe. If 380 mm Hg (12 in. Hg) is exceeded during the test, either leak check at this higher vacuum or end the leak check as described below and start the test over.

When the leak check is completed, first slowly remove the TFE® plug from the inlet to the probe then immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the probe.

10.1.3.2 Leak Checks During a Test

A leak check shall be performed before and after a change of port during a test. A leak check shall be performed before and after a component (e.g., filter or optional water knockout trap) is changed during a test.

Such leak checks shall be performed according to the procedure given in Section 10.1.3.1 of this method except that it shall be performed at a vacuum equal to or greater than the highest value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 ft^3/min) or 4% of the average sampling rate (whichever is smaller) the results are acceptable. If, however, a higher leakage rate is observed, the tester shall either: (1) record the leakage rate and then correct the volume of gas sampled since the last leak check as shown in Section 10.1.3.4 of this method, or (2) void the test.

10.1.3.3 Post-Test Leak Check

A leak check is mandatory at the end of a test. This leak check shall be performed in accordance with the procedure given in Section 10.1.3.1 except that it shall be conducted at a vacuum equal to or greater than the highest value recorded during the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 ft^3/min) or 4% of the average sampling rate (whichever is smaller), the results are acceptable. If, however, a higher leakage rate is observed, the tester shall either: (1) record the leakage rate and correct the volume as gas sampled since the last leak check as shown in Section 10.1.3.4 of this method, or (2) void the test.

10.1.3.4 Correcting for Excessive Leakage Rates

The equation given in Section 11.3 of this method for calculating V_m(std), the corrected volume of gas sampled, can be used as written unless the leakage rate observed during any leak check after the start of a test exceeded L_a, the maximum acceptable leakage rate (see definitions below). If an observed leakage rate exceeds L_a, then replace V_m in the equation in Section 11.3 with the following expression:

$$[V_m - \sum_{i=1}^{n} (L_i - L_a)\,\theta_i - L_p - L_a)\,\theta_p]$$

where:

V_m - Volume of gas sampled as measured by the dry gas meter (dscf).

L_a - Maximum acceptable leakage rate equal to 0.00057 m^3/min. (0.02 ft^3/min) or 4% of the average sampling rate, whichever is smaller.

L_p - Leakage rate observed during the post-test leak check, m^3/min (ft^3/min).

L_i - Leakage rate observed during the leak check performed prior to the "i th" leak check (i = 1,2,3...n), m^3/min (ft^3/min).

θ_i - Sampling time interval between two successive leak checks beginning with the interval between the first and second leak checks, min.

θ_p - Sampling time interval between the last (n th) leak check and the end of the test, min.

Substitute only for those leakages (L_i or L_p) which exceeded L_a.

10.1.3.5 Train Operation

During the sampling run, a sampling rate within 10% of the selected sampling rate shall be maintained. Data will be considered acceptable if readings are recorded at least every 5 min. and not more than 10% of the point readings are in excess of ±10% and the average of the point readings is within ±10%. During the run, if it becomes necessary to change any system component in any part of the train, a leak check must be performed prior to restarting.

For each run, record the data required on the data sheets. An example is shown in Fig. 4. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment and when sampling is halted.

To begin sampling, remove the nozzle cap, verify (if applicable) that the probe and sorbent module temperature control systems are working and at temperature and that the probe is properly positioned. Position the probe at the sampling point. Immediately start the pump and adjust the flow rate.

If the stack is under significant sub-ambient pressure (height of impinger stem), take care to close the coarse adjust valve before inserting the probe into the stack to avoid water backing into the probe. If necessary, the pump may be turned on with the coarse adjust valve closed.

During the test run, make periodic adjustments to keep the probe temperature at the proper value. Add more ice and, if necessary, salt to the ice bath. Also, periodically check the level and zero of the manometer and maintain the temperature of sorbent module at or less than 20°C but above 0°C.

If the pressure drop across the train becomes high enough to make the sampling rate difficult to maintain, the test run shall be terminated unless the replacing of the filter corrects the problem. If the filter is replaced, a leak check shall be performed.

At the end of the sample run, turn off the pump, remove the probe and nozzle from the stack, and record the final dry gas meter reading. Perform the post test leak check.*

*With acceptability of the test run to be based on the same criterion as in 10.1.3.1.

FIELD DATA

PLANT ____________
DATE ____________
SAMPLING LOCATION ____________
SAMPLE TYPE ____________
RUN NUMBER ____________
OPERATOR ____________
BAROMETRIC PRESSURE ____________
SITE TO BARO. ELEVATION (H_s) ____________
CORRECTED B.P. ____________
STATIC PRESSURE (P_s) ____________
FILTER NUMBER(s) ____________

PROBE LENGTH AND TYPE ____________
NOZZLE I.D. ____________
ASSUMED MOISTURE, % ____________
SAMPLE BOX NUMBER ____________
METER BOX NUMBER ____________
TEMPERATURE METER NO ____________
THERMOCOUPLE I.D. NO ____________
METER ΔH ____________
METER CORRECTION ____________
C FACTOR ____________
REFERENCE ΔP ____________
UMBILICAL CORD I.D. NO ____________

SCHEMATIC OF TRAVERSE POINT LAYOUT
Read and Record All Data
Every ______ Minutes

LEAK CHECK: Initial at ≥ 15" Hg CFM ______
Final at ______ "Hg CFM ______
Pitot at ≥ 3" H_2O ______

$$Vm_1 = \_\_\_\_\_\_ (Tm + 460) \sqrt{\frac{\Delta Ps}{Ts + 460}}$$

TRAVERSE POINT NUMBER	SAMPLING TIME, min	CLOCK TIME (24 hr CLOCK)	GAS METER READING (V_m), ft³		VELOCITY HEAD (Δp_s), in. H_2O	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O		STACK TEMPERATURE (T_s),°F	DRY GAS METER TEMPERATURE		PUMP VACUUM, in. Hg	SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
			DESIRED	ACTUAL		DESIRED	ACTUAL		INLET ($T_{m_{in}}$),°F	OUTLET ($T_{m_{out}}$),°F		XAD-2	

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10.2 Sample Recovery

Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period.

When the probe can be safety handled, wipe off all external particulate matter near the tip of the probe. Remove the probe from the train and close off both ends with hexane-rinsed aluminum foil. Seal off the inlet to the train with a ground glass cap or hexane-rinsed aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area should be clean and enclosed so that the chances of contaminating or losing the sample will be minimized. No smoking shall be allowed.

Inspect the train prior to and during disassembly and note any abnormal conditions, e.g., broken filters, color of the impinger liquid, etc. Treat the samples as follows:

10.2.1 Container No. 1

Either seal the ends of the filter holder or carefully remove the filter from the filter holder and place it in its identified container. Use a pair of precleaned tweezers to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and/or filter fibers which adhere to the filter holder gasket, by using a dry inert bristle brush and/or a sharp-edged blade. Seal the container.

10.2.2 Sorbent Modules

Remove the sorbent module from the train and cap it off.

10.2.3 Cyclone Catch

If the optional cyclone is used, quantitatively recover the particulate into a sample container and cap.

10.2.4 Sample Container No. 2

Quantitatively recover material deposited in the nozzle, probe, transfer line, the front half of the filter holder, and the cyclone, if used, first by brushing and then by sequentially rinsing with acetone and then hexane three times each and add all these rinses to Container No. 2. Mark level of liquid on container.

10.2.5 Sample Container No. 3

Rinse the back half of the filter holder, the connecting line between the filter and the condenser and the condenser (if using the separate condenser-sorbent trap) three times each with acetone exane collecting all rinses in Container 3. If using the ned condenser-sorbent trap, the rinse of the condenser shall rformed in the laboratory after removal of the XAD-2. If the nal water knockout trap has been employed, it shall be ed and recorded and its contents placed in Container 3 along the rinses of it. Rinse it three times each with acetone, exane. Mark level of liquid on container.

6 Sample Container No. 4

emove the first impinger. Wipe off the outside of the ger to remove excessive water and other material, weigh (stem ded), and record the weight on data sheet. Pour the contents inses directly into Container No. 4. Rinse the impinger ntially three times with acetone, and hexane. Mark level of d on container.

.7 Sample Container No. 5

Remove the second and third impingers, wipe the outside to re excessive water and other debris, weigh (stem included) and rd weight on data sheet. Empty the contents and rinses into ainer No. 5. Rinse each with distilled DI water three times. level of liquid on container.

.8 Silica Gel Container

Remove the last impinger, wipe the outside to remove excessive r and other debris, weigh (stem included), and record weight ata sheet. Place the silica gel into its marked container.

CALCULATIONS

Carry out calculations, retaining at least one extra decimal re beyond that of the acquired data. Round off figures after l calculations.

Nomenclature

C_s - Total weight of chlorinated organic compounds in stack gas sample, ng.

C_s - Concentration of chlorinated organic compounds in stack gas, μg/m^3, corrected to standard conditions of 20°C, 760 mm Hg (68°F, 29.92 in. Hg) on dry basis.

A_n - Cross-sectional area of nozzle, m^2 (ft^2).

B_{ws} - Water vapor in the gas stream, proportion by volume.

I - Percent of isokinetic sampling.

M_w - Molecular weight of water, 18 g/g-mole (18 lb/lb-mole)

P_{bar} - Barometric pressure at the sampling site, mm Hg (in. Hg).

P_s - Absolute stack gas pressure, mm Hg (in. Hg).

P_{std} - Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R - Ideal gas constant, 0.06236 mm Hg-m^3/°K-g-mole (21.83 in. Hg-ft^3/°R-lb-mole).

T_m - Absolute average dry gas meter temperature °K (°R).

T_s - Absolute average stack gas temperature °K (°R).

T_{std} - Standard absolute temperature, 293°K (68°F).

m_{lc} - Total mass of liquid collected in impingers and silica gel.

V_m - Volume of gas sample as measured by dry gas meter, dcm (dcf).

$V_m(std)$ - Volume of gas sample measured by the dry gas meter corrected to standard conditions, dscm (dscf).

$V_w(std)$ - Volume of water vapor in the gas sample corrected to standard conditions, scm (scf).

v_s - Stack gas velocity, calculated by combustion calculation, m/sec (ft/sec).

Y - Meter box correction factor.

ΔH - Average pressure differential across the orifice meter, mm H_2O (in. H_2O).

θ - Total sampling time, min.

13.6 - Specific gravity of mercury.

60 - Sec/min.

100 - Conversion to percent.

11.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop

See data sheet (Fig. 5).

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11.3 Dry Gas Volume

Correct the sample volume measured by the dry gas meter to standard conditions [20°C, 760 mm Hg (68±F, 29.92 in. HG)] by using Equation 1.

$$V_m(std) = Y\, V_m \frac{T_{std}}{T_m} \frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}} = K_1 V_m \frac{P_{bar} + \frac{\Delta H}{13.6}}{T_m} \qquad (1)$$

where:

K_1 = 0.3855 °K/mm Hg for metric units

= 17.65 °R/in. Hg for English units

11.4 Volume of Water Vapor

$$V_w(std) = m_{lc} \frac{RT_{std}}{M_w \times P_{std}} = K_2 m_{lc} \qquad (2)$$

where:

K_2 = 0.00134 m^3/ml for metric units

= 0.0472 ft^3/ml for English units

11.5 Moisture Content

$$B_{ws} = \frac{V_w(std)}{V_m(std) + V_w(std} \qquad (3)$$

If liquid droplets are present in the gas stream assume the stream to be saturated and use a psychrometric chart to obtain an approximation of the moisture percentage.

11.6 Percent Isokinetic Sampling

$$I = \frac{100\, T_s\, [K_4\, m_{lc} + (V_m\, Y_m)\, (P_{bar} + \Delta H/13.6)]}{60\, \theta_{vs}\, P_s\, A_n} \qquad (4)$$

where:

K_4 = 0.003454 mm Hg - m^3/ml - °K for metric units

= 0.002669 in Hg - ft^3/ml - °R for English units

11.7 Concentration of Chlorinated Organic Compounds in Stack Gas

Determine the concentration of chlorinated organic compounds in the stack gas according to Equation 5.

$$C_s = K_3 \frac{C_a}{V_m(std)} \qquad (5)$$

where:

K_3 = 35.31 ft^3/m^3

12. QUALITY ASSURANCE (QA) PROCEDURES

The positive identification and quantification of specific compounds in this assessment of stationary conventional combustion sources is highly dependent on the integrity of the samples received and the precision and accuracy of all analytical procedures employed. The QA procedures described in this section were designed to monitor the performance of the sampling methods and to provide information to take corrective actions if problems are observed.

Field Blanks

The field blanks should be submitted as part of the samples collected at each particular testing site. These blanks should consist of materials that are used for sample collection and storage and are expected to be handled with exactly the same procedure as each sample medium.

Blank Train

For each series of test runs, set up a blank train in a manner identical to that described above, but with the probe inlet capped with hexane-rinsed aluminum foil and the exit end of the last impinger capped with a ground glass cap. Allow the train to remain assembled for a period equivalent to one test run. Recover the blank sample as described in Sec. 7.2.

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ANALYTICAL PROCEDURES TO ASSAY STACK EFFLUENT SAMPLES AND RESIDUAL COMBUSTION PRODUCTS FOR POLYCHLORINATED DIBENZO-p-DIOXINS (PCDD) AND POLYCHLORINATED DIBENZOFURANS (PCDF)

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Sponsored By

THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS, U.S. DEPARTMENT OF ENERGY AND U.S. ENVIRONMENTAL PROTECTION AGENCY

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Scope and Applicability of Method

The analytical procedures described here are applicable for the ermination of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzo- ans (PCDF) in stack effluents from combustion processes. These methods also applicable to residual combustion products such as bottom and cipitator ash. The methods presented entail addition of isotopically- eled internal standards to all samples in known quantities, extraction the sample with appropriate organic solvents, preliminary fractionation cleanup of the extracts using a sequence of liquid chromatography umns, and analysis of the processed extract for PCDD and PCDF using pled gas chromatography - mass spectrometry (GC-MS). Various formance criteria are specified herein which the analytical data t satisfy for quality assurance purposes. These represent minimum teria which must be incorporated into any program in which PCDD PCDF are determined in combustion product samples.

The method presented here does not yield definitive information on concentration of individual PCDD/PCDF isomers, except for 2,3,7,8- rachlorodibenzo-p-dioxin (TCDD) and 2,3,7,8-Tetrachlorodibenzofuran DF). Rather, it is designed to indicate the total concentration of isomers of several chlorinated classes of PCDD/PCDF (that is, total ra-, penta-, hexa-, hepta-, and octachlorinated dibenzo-p-dioxins and enzofurans). Of the 75 separate PCDD and 135 PCDF isomers, there 22 TCDD, 38 TCDF, 14 PeCDD, 28 PeCDF, 10 HxCDD, 16 HxCDF, 2 HpCDD, pCDF, 1 OCDD and 1 OCDF.[a]

The analytical method presented herein is intended to be applicable determining PCDD/PCDF present in combustion products at the ppt to level, but the sensitivity which can ultimately be achieved for a en sample will depend upon the types and concentrations of other chemical pounds in the sample.

The method described here must be implemented by or under the ervision of chemists with experience in handling supertoxic materials analyses should only be performed in rigorously controlled, limited ess laboratories. The quantitation of PCDD/PCDF should be accomplished y by analysts experienced in utilizing capillary-column gas chromatography- s spectrometry to accomplish quantitation of chlorocarbons and similar pounds at very low concentration.

The toxicological data which are available for the PCDD and PCDF are far from complete. That is, the toxicological properties of all of the isomers comprising the 75 possible PCDD and 135 possible PCDF are not presently known. However, a considerable body of toxicological data exists for 2,3,7,8-TCDD which indicates that, in certain animal species, this compound is lethal at extraordinarily low does and causes a wide range of systemic affects, including hepatic disorders, carcinoma and birth defects. While much less data is available regarding the toxicology of 2,3,7,8-TCDF, sufficient data is available to form the basis for the belief that 2,3,7,8-TCDF is similar in its toxicological properties to 2,3,7,8-TCDD. Relatively little is known about the toxicology of the higher chlorinated PCDD and PCDF (that is, penta through octachlorinated PCDD/PCDF), although there is some data to suggest that certain penta-, hexa-, and hepta- PCDD/PCDF isomers are hazardous. In view of the extraordinary toxicity of 2,3,7,8-TCDD and in view of the exceptional biological activity of this compound (on the basis of enzyme induction assays) and of compounds having similar molecular structures, extensive precautions are required to preclude exposure to personnel during handling and analysis of materials containing these compounds and to prevent contamination of the laboratory. Specific safety and handling procedures which are recommended are given in the Appendix to this protocol.

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[a] The abbreviations which are used to designate chlorinated dibenzo-p-dioxins and dibenzofurans throughout this document are as follows:

PCDD - Any or all of the 75 possible chlorinated dibenzo-p-dioxin isomers

PCDF - Any or all of the 135 possible chlorinated dibenzofuran isomers

TCDD - Any or all of the 22 possible tetrachlorinated dibenzo-p-dioxin isomers

TCDF - Any or all of the 138 possible tetrachlorinated dibenzofuran isomers

PeCDD - Any or all of the 14 possible pentachlorinated dibenzo-p-dioxin isomers

PeCDF - Any or all of the 28 possible pentachlorinated dibenzofuran isomers

HxCDD - Any or all of the 10 possible hexachlorinated dibenzo-p-dioxin isomers

HXCDF - Any or all of the 16 possible hexachlorinated dibensofuran isomers

HpCDD - Any or all of the 2 possible heptachlorinated dibenzo-p-dioxin isomers

HpCDF - Any or all of the 4 possible heptachlorinated dibenzofuran isomers

OCDD - Octachlorodibenzo-p-dioxin

OCDF - Octachlorodibenzofuran

Specific Isomers. - Any of the abbreviations cited above may be converted to designate a specific isomer by indicating the exact positions (carbon atoms) where chlorines are located within the molecule. For example, 2,3,7,8-TCDD refers to only one of the 22 possible TCDD isomers - that isomer which is chlorinated in the 2,3,7,8 positions of the dibenzo-p-dioxin ring structure.

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2. Reagents and Chemicals

The following reagents and chemicals are appropriate for use in these procedures. In all cases, equivalent materials from other suppliers may also be used.

2.1 Potassium Hydroxide, Anhydrous, Granular Sodium Sulfate and Sulfuric Acid (all Reagent Grade): J. T. Baker Chemical Co. or Fisher Scientific Co. The granular sodium sulfate is purified prior to use by placing a beaker containing the sodium sulfate in a 400°C oven for four hours, then removing the beaker and allowing it to cool in a desiccator. Store the purified sodium sulfate in a bottle equipped with a Teflon-lined screw cap.

2.2 Hexane, Methylene Chloride, Benzene, Methanol, Toluene, Isooctane: "Distilled in Glass" Burdick and Jackson.

2.3 Tridecane (Reagent Grade): Sigma Chemical Co.

2.4 Basic Alumina (Activity Grade 1, 100 - 200 mesh): ICN Pharmaceuticals. Immediately prior to use, the alumina is activated by heating for at least 16 hours at 600°C in a muffle furnace and then allowed to cool in a desiccator for at least 30 minutes prior to use. Store pre-conditioned alumina in a desiccator.

2.5 Silica (Bio-Sil A.100/200 mesh): Bio-Rad. The following procedure is recommended for conditioning the Bio-Sil A prior to use. Place an appropriate quantity of Bio-Sil A in a 30 mm x 300 mm long glass tube (the silica gel is held in place by glass wool plugs) which is placed in a tube furnace. The glass tube is connected to a pre-purified nitrogen cylinder, through a series of four traps (stainless steel tubes, 1.0 cm O.D. x 10 cm long)[6]: 1) Trap No. 1 - Mixture comprised of Chromosorb W/AW (60/80 mesh coated with 5% Apiezon L), Graphite (UCP-1-100), Activated Carbon (50 to 200 mesh) in a 7:1.5:1.5 ratio (Chromosorb W/AW, Apiezon L obtained from Supelco, Inc., Graphite obtained from Ultracarbon Corporation, 100 mesh, 1-M-USP; Activated Carbon obtained from Fisher Scientific Co.); 2) Trap No. 2 - Molecular Sieve 13 X (60/80 mesh), Supelco, Inc.; 3) Trap No. 3 - Carbosieve S (80/100 mesh), obtained from Supelco, Inc.; 4) The Bio-Sil A is heated in the tube for 30 minutes at 180°C while purging with nitrogen (flow rate 50-100 mL/minute), and the tube is then removed from the furnace and allowed to cool to room temperature. Methanol (175 mL) is then passed through the tube, followed by 175 mL methylene chloride. The tube containing the silica is then returned to the furnace, the nitrogen purge is again established (50-100 mL flow) and the tube is heated at 50°C for 10 minutes, then the temperature is gradually increased to 180°C over 25 minutes and maintained at 180°C for 90 minutes. Heating is then discontinued but the nitrogen purge is continued until the tube cools to room temperature. Finally, the silica is transferred to a clean, dry, glass bottle and capped with a Teflon-lined screw cap for storage.

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2.6 Silica Gel Impregnated With Sulfuric Acid: Concentrated sulfuric acid (44 g) is combined with 100 g Bio-Sil A (conditioned as described above) in a screw capped bottle and agitated to mix thoroughly. Aggregates are dispersed with a stirring rod until a uniform mixture is obtained. The H_2SO_4-silica gel is stored in a screw-capped bottle (Teflon-lined cap).

2.7 Silica Gel Impregnated with Sodium Hydroxide: 1N Sodium hydroxide (39 g) is combined with 100 g Bio-Sil A (conditioned as described above) in a screw capped bottle and agitated to mix throughly. Aggregates are dispersed with a stirring rod until a uniform mixture is obtained. The NaOH-silica gel is stored in a screw-capped bottle (Teflon-lined cap).

2.8 Carbon/Celite:
Carbon: AX-21 Carbon, Anderson Development Co., Adrian, Mich. 49221
Celite 545: Fisher Scientific Co

Combine AX-21 Carbon (10.7 g) with Celite 545 (124 g) in a 250 mL glass bottle fitted with a Teflon-lined cap. Agitate the mixture to combine thoroughly. Store in the screw-capped bottle.

2.9 Sepralyte Diol (40µ): Analytichem International

2.10 Nitrogen and Hydrogen (Ultra High Purity): Matheson Scientific

3. Apparatus and Materials

The following apparatus and materials are appropriate for use in these procedures. In all cases, equivalent items from other suppliers may also be used.

3.1 Glassware used in the analytical procedures (including the Soxhlet apparatus and disposable bottles) is cleaned by rinsing successively three times with methanol and then three times with methylene chloride, and finally drying it in a 100°C oven. Bottles cleaned in this manner are allowed to cool to room temperature and are then capped using Teflon-lined lids. Teflon cap liners are rinsed as just described but are allowed to air-dry. More rigorous cleaning of some glassware with detergent may be required prior to the solvent rinses, for example, the glassware employed for Soxhlet extraction of samples.

3.1.1 Sample Vessels: 125 mL and 250 mL flint glass bottles fitted with screw caps and teflon cap liners, and glass test tubes, VWR-Scientific.

3.1.2 Teflon Cap Liners: Scientific Specialities Service, Inc.

3.1.3 Soxhlet Apparatus: Extraction apparatus, Allihn condenser, Kimax Brand, American Scientific Products Cat. No. E6252-2A.

3.1.4 Gravity Flow Liquid Chromatographic Columns: Custom Fabricated Details of the columns are provided in later sections).

3.1.5 Micro-vials (3.0 mL): Reliance Glass.

3.2 Capillary Gas Chromatographic Columns: Two different columns are required if data on both 2,3,7,8-TCDD and 2,3,7,8-TCDF, as well as on the total PCDD/PCDF by chlorinated class, are desired. The appropriate columns are: 1) A fused silica column (60 M x 0.25 mm I.D.) coated with DB-5 (0.25 μ film thickness), J & W Scientific, Inc., Rancho Cordova, Calif., is utilized to separate each of the several tetra-through octachlorinated CDDs and CDFs, as a group, from all of the other groups. While this column does not resolve all of the isomers within each chlorinated group, it effectively resolves each of the chlorinated groups from all of the other chlorinated groups and therefore provides data on the total concentration of each group (that is, total tetra-, penta-, hexa-, hepta- and octa CDDs and CDFs). This column also resolves 2,3,7,8-TCDD from all of the other 21 TCDD isomers and this isomer can therefore be determined quantitatively if proper calibration procedures are applied as described further in a later section. This column does not completely resolve 2,3,7,8-TCDF from the other TCDF isomers, and if a peak corresponding in retention time to 2,3,7,8-TCDF is observed in the analysis using this column, then a portion of the sample extract must be reanalyzed using the second GC column described below if isomer - specific data on 2,3,7,8-TCDF is desired. 2) A fused silica column (30 M x 0.25 mm I.D.) coated with DB-225 (0.25 μ film thickness), J & W Scientific, Inc., Rancho Cordova, Calif., must be utilized to obtain quantitative data on the concentration of 2,3,7,8-TCDF, since this column adequately resolves 2,3,7,8-TCDF from the other TCDF isomers.

3.3 Balance: Analytical Balance, readibility, 0.0001 g.

3.4 Nitrogen Blowdown Concentration Apparatus: N-Evap Analytical Evaporator Model III, Organomation Associates Inc.

3.5 Tube Furnace: Lindberg Type 59344.

4. Instrumentation

Gas Chromatograph-Mass Spectrometer-Data System (GC/MS/DS): The instrument system used to analyze sample extracts for PCDD/PCDF comprises a gas chromatograph (fitted for capillary columns) coupled directly or through an enrichment device to a mass spectrometer which is equipped with a computer-based data system. The individual components of the GC/MS/DS are described below.

4.1 Gas Chromatograph (GC): The chromatograph must be equipped with an appropriate injector and pneumatic system to permit use of the specified glass or fused silica capillary columns. It must also incorporate an oven which can be heated in a reproducible, programmed temperature cycle. The injector should be configured for splitless/split injections. The GC column performance should be verified at the beginning of each 8 hour work period or at the beginning of each series of analyses if more than one set of samples is analyzed during an 8 hour shift. Extracts of complex combustion products and effluents may contain numerous organic residues even after application of the extensive prefractionation/cleanup procedures specified in this method. These residues may result in serious deviation of GC column performance and therefore, frequent performance checks are desirable. Using appropriate calibration mixtures, as described below, the retention time windows for each chlorinated class of CDDs/CDFs must be verified. In addition, the GC column utilized must be demonstrated to effectively separate 2,3,7,8-TCDD from all other TCDD isomers if data on 2,3,7,8-TCDD alone is desired with at least 20% valley definition between the 2,3,7,8- isomer and the other adjacent-eluting TCDD isomers. Typically, capillary column peak widths (at half-maximum peak height) on the order of 5-10 seconds are obtained in the course of these analyses. An appropriate GC temperature program for the analyses described herein is discussed in a later section (see Table 1).

4.2 Gas Chromatograph-Mass Spectrometer Interface: The GC-MS interface can include enrichment devices, such as a glass jet separator or a silicone membrane separator, or the gas chromatograph can be directly coupled to the mass spectrometer source, if the system has adequate pumping of the source region. The interface may include a diverter valve for shunting the column effluent and isolating the mass spectrometer source. All components of the interface should be glass or glass-lined stainless steel. The interface components must be compatible with temperatures in the neighborhood of 250°C, which is the temperature at which the interface is typically maintained throughout analyses for PCDD/PCDF. The GC/MS interface must be appropriately configured so that the separation of 2,3,7,8-TCDD from the other TCDD isomers which is achieved in the gas chromatographic column is not appreciably degraded. Cold spots and/or active surfaces (adsorption sites) in the GC/MS interface can cause peak tailing and peak broadening. If the latter are observed, thorough cleaning of the injection port, interface and connecting lines should be accomplished prior to proceeding.

4.3 Mass Spectrometer (MS): The mass spectrometer used for the analyses described here is typically a double-focusing sector or quadrupole instrument equipped with an electron impact source (70 ev), maintained at 250°C, and a standard electron multiplier detector. If possible, it is desirable to have both low and high resolution capability with the mass spectrometer used, since confirmation of data obtained by low resolution MS using high resolution MS is sometimes desirable. Alternatively, a combination of mass spectrometers can be used for this purpose. The static resolution of the instrument must be maintained at a minimum of 1:500 (with a 10% valley between adjacent masses) if operating in the low resolution MS mode, and a minimum resolution of 1:10,000 is desirable for operation in the high resolution mode. The mass spectrometer must also be configured for rapid computer-controlled selected-ion monitoring in both high and low resolution operating modes. At a minimum, two ion-masses characteristic of each class of chlorinated dioxins should be monitored, and these are two ions in the molecular ion isotopic cluster. It is desirable for increased confidence in the data to also monitor the fragment ions arising from the loss of COCl from the molecular ion. In order to accomplish the requisite rapid multiple ion monitoring sequence during the time period defined by a typically capillary chromatographic peak (the base of the chromatographic peak is typically 15-20 seconds in width), the following MS performance parameters are typically required (assuming a 4-ion monitoring sequence for each class of PCDD/PCDF): dwell time/ion-mass, ≈100 msec.; minimum number of data points/chromatographic peak, 7 . The mass scale of the mass spectrometer is calibrated using high boiling perfluorokerosene and/or some other suitable mass standard depending upon the requirements of the GC-MS-DS system utilized. The actual procedures utilized for calibration of the mass scale will be unique to the particular mass spectrometer being employed. A list of the appropriate ions to be monitored in the PCDD/PCDF analyses described herein is presented in a later section (see Table 1).

4.4 Data System: A dedicated computer-based data system, capable of providing the data described above, is employed to control the rapid selected-ion monitoring sequence and to acquire the data. Both digital data (peak areas or peak heights) as well as peak profiles (displays of intensities of ion-masses monitored as a function of time) should be acquired during the analyses, and displayed by the data system. This raw data (mass chromatograms) should be provided in the report of the data.

5. Calibration Standards

A recommended set of calibration standards to be used in the analyses described herein is presented below. Stock standard solutions of the various PCDD and PCDF isomers and mixtures thereof are prepared in a glovebox, using weighed quantities of the authentic isomers.[b] These stock solutions are contained in appropriate volumetric flasks and are stored tightly stoppered, in a refrigerator. Aliquots of the stock standards are removed for direct use or for subsequent serial dilutions to prepare working standards. These standards must be checked regularly (by comparing instrument response factors for them over a period of time) to ensure that solvent evaporation or other losses have not occurred which would alter the standard concentration. The several recommended standard solutions are as follows.

5.1 Standard Mixture A: Prepare a stock solution containing the following isotopically-labelled PCDD and PCDF in isooctane at the indicated concentrations: 2.5ng./µl $^{13}C_{12}$-2,3,7,8-TCDD, 2.5ng/µl $^{37}Cl_4$-2,3,7,8-TCDF, 25ng/µL $^{13}C_{12}$-1,2,3,4,7,8-HxCDD, 25ng/µL $^{13}C_{12}$-1,2,3,4,7,8-HxCDF, 25ng/µL $^{13}C_{12}$-OCDD, and 25ng/µL $^{13}C_{12}$-OCDF. Portions of this isomer mixture are added to all samples prior to analyses and serve as internal standards for use in quantitation. Recovery of these standards is also used to guage the overall efficacy of the analytical procedures.

5.2 Standard B: Prepare a stock solution containing 1.0 ng of $^{37}Cl_4$-2,3,7,8-TCDD/µL of isooctane. This standard can be coinjected if desired, along with aliquots of the final sample extract to reliably estimate the recovery of the $^{13}C_{12}$-2,3,7,8-TCDD surrogate standard.

5.3 Standard Mixture C: Prepare a stock solution containing 100 ng/µL of isooctane of each of the following PCDD and PCDF: 2,3,7,8-TCDF; 2,3,7,8-TCDD; 1,3,4,6,8-PeCDF, 2,3,4,6,7-PeCDF; 1,2,4,7.9-PeCDD; 1,2,3,8,9-PeCDD; 1,2,3,4,6,8-HxCDF; 2,3,4,6,7,8-HxCDF; 1,2,3,4,6,8-HxCDD, 1,2,3,4,6,7-HxCDD; 1,2,3,4,6,7,8-HpCDF; 1,2,3,4,7,8,9-HpCDF; 1,2,3,4,6,7,8-HpCDD; 1,2,3,4,6,7,9-HpCDD; OCDF: and OCDD. This isomer mixture is used to define the gas chromatographic retention time intervals or windows for each of the penta-, hexa-, hepta-, and octachlorinated groups of PCDD and PCDF. Each pair of isomers of a given chlorinated class which is listed here corresponds to the first and last eluting isomers of that class on the DB-5 capillary GC column (except for TCDD and TCDF). In addition, this isomer mixture is used to determine GC-MS response factors for representative isomers of each of the penta-, hexa-, hepta-, and octachlorinated groups of PCDD and PCDF. The later data are used in quantitating the analytes in unknown samples.

5.4 Standard Mixture D: Prepare a stock solution containing 50 pg/µL of isooctane of each of the following TCDD isomers: 1,3,6,8-TCDD; 1,2,3,7-TCDD; 1,2,3,9-TCDD; 2,3,7,8-TCDD; and 1,2,8,9-TCDD. Two of the isomers in this mixture are used to define the gas chromatographic retention time window for TCDDs (1,3,6,8-TCDD is the first eluting TCDD isomer and 1,2,8,9-TCDD is the last eluting TCDD isomer on the DB-5 GC column). The remaining isomers serve to demonstrate that the 2,3,7,8-TCDD isomer is resolved from the other nearest eluting TCDD isomers, and that the column therefore yields quantitative data for the 2,3,7,8-TCDD isomer alone.

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[b] Some of the PCDD/PCDF isomer standards recommended for this method are available from Cambridge Isotope Laboratories, Cambridge, Massachusetts. Other PCDD/PCDF standards are available from the Brehm Laboratory, Wright State University, Dayton, Ohio, from the U.S. EPA Standard Repository at Research Triangle Park, North Carolina and possibly from other laboratories Not all of the indicated isotopically-labelled PCDD/PCDF internal standards recommended here are presently available in quantities sufficient for widespread distribution, but these are expected to be available in the near future.

5.5 Standard Mixture E: Prepare a stock solution containing 50 pg/ul of isooctane of each of the following TCDF isomers: 1,3,6,8-TCDF; 2,3,4,8-TCDF; 2,3,7,8-TCDF, 2,3,4,7-TCDF; and 1,2,8,9-TCDF. This isomer mixture is used to define the TCDF gas chromatographic retention time window (1,3,6,8- and 1,2,8,9-TCDF are the first and last eluting TCDFs on the DB-5 capillary column) and to demonstrate that 2,3,7,8-TCDF is uniquely resolved from the adjacent-eluting TCDF isomers.

6. Procedures for Addition of Internal Standards and Extraction of Samples

Both liquid and solid samples will be obtained for PCDD/PCDF analyses as a result of the application of an appropriate stack sampling procedure. Samples resulting from the sampling train will include the following (these will be provided to the analytical laboratory as separate samples in the form indicated): 1) particulate filter and particulates thereon; 2) particulates from the cyclone (if used); 3) combined aqueous solutions from the impingers; 4) the intact XAD-resin cartridge and the resin therein; 5) combined aqueous rinse (if used) solutions from rinses of the nozzle, probe, filter holder, cyclone (if used), impingers, and all connecting lines; 6) combined acetone rinse solutions from rinses of the nozzle, probe, filter holder, cyclone (if used), impingers, and all connecting lines; 7) combined hexane rinse solutions from rinses of the nozzle, probe, filter, cyclone (if used), impingers, and all connecting lines. In addition, samples of bottom ash, precipitator ash, incinerator feed materials or fuel, quench liquids, and materials from effluent control devices may also be provided for analyses.

In general, the volumes of all liquid samples received for analyses are measured and recorded, and where appropriate, solid samples or aliquots thereof are weighed. Any samples which are homogeneous (as for example, a single liquid phase sample or a solid which can be thoroughly mixed) can be split prior to analyses, if desired, provided that this will still permit the attainment of the desired detection limits for the analytes of interest. Samples such as particulates from the sampling train which are generally collected in relatively small quantity, are preferably analyzed in total.

6.1 Organic Liquid Samples (Acetone and Hexane Solutions). Combine the acetone and hexane rinse solution and concentrate to a volume of about 1-5 mL using the nitrogen blowdown apparatus (a stream of dry nitrogen)

while heating the sample gently on a water bath. Rinse the vessels which contained the original solutions three times with small portions of hexane and add these to the concentrated solutions and concentrate further to near dryness. This residue will likely contain particulates which were removed in the rinses of the train probe and nozzle. Combine the residue (along with three rinses of the final sample vessel) in the Soxhlet apparatus with the filter and particulates, and proceed as described under Solid Sample below.

6.2 Aqueous Liquids

Add an appropriate quantity of the isotopically-labeled internal standard mixture (Standard Mixture A described earlier) to the aqueous liquid sample (or an aliquot thereof) in a screw-capped bottle fitted with a Teflon-lined cap. Add approximately 25% by volume of hexane to the spiked aqueous sample, seal the bottle and agitate on a shaker for a period of three hours. Allow the vessel to stand until the aqueous and organic layers separate, then transfer the organic layer to a separate sample bottle. Repeat the hexane extraction sequence two additional times and combine the organic fractions with that from the first extraction. Proceed with the sample fractionation and cleanup procedures described below.

6.3 Solid Samples

Place a glass extraction thimble and 1 g of silica gel and a plug of glass wool into the Soxhlet apparatus, charge the apparatus with toluene and reflux for a period of one hour. Remove the toluene and discard it, retaining the silica gel, or if desired, retain a portion of the toluene to check for background contamination. For extraction of particulates, place the entire sample in the thimble onto the bed of precleaned silica gel (1 cm. thick), and top with the precleaned glass wool retained from the initial Soxhlet cleaning procedure. Add the appropriate quantity of the isotopically-labelled internal standard mixture (Standard Mixture A described earlier) to the sample in the Soxhlet thimble. Charge the Soxhlet with toluene and reflux for a period of 16 hours. After extraction, allow the Soxhlet to cool, remove the toluene extract, and transfer it to another sample vessel. Concentrate the extract to a volume of approximately 40 ml by using the nitrogen blowdown apparatus described earlier. Proceed with the sample fractionation and cleanup procedures described below.

7. Procedures for Cleanup and Fractionation of Sample Extracts

The following column chromatographic sample clean-up procedures are used in the order given, although not all may be required. In general, the silica and alumina column procedures are considered to be a minimum requirement. Acceptable alternative cleanup procedures may be used provided that they are demonstrated to effectively transmit a

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epresentative set of the analytes of interest. The column chromato-raphic procedures listed here have been demonstrated to be effective or a mixture consisting of 1,2,3,4-TCDD, 2,3,7,8-TCDD, 2,3,6,8-TCDF, ,2,4,8-TCDF, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDD, 1,2,4,7,8-PeCDF, 1,2,3,4,7,8-xCDD, 1,2,4,6,7.9-HxCDF, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,8,9-HpCDF, CDD and OCDF

An extract obtained as described in the foregoing sections is oncentrated to a volume of about 1 mL using the nitrogen blowdown pparatus, and this is transferred quantitatively (with rinsings) to the combination silica gel column described below.

7.1 Combination Silica Gel Column: Pack one end of a glass column (20 mm. O.D. x 230 mm in length) with glass wool (precleaned) and add, in sequence, 1 g silica gel, 2 g base-modified silica gel, 1 g silica gel, 4 g acid-modified silica gel, and 1 g silica gel. (Silica gel and modified silica gel are prepared as described in the Reagents sections of this protocol.) Preelute the column with 30 mL hexane and discard the eluate. Add the sample extract in 5 mL of hexane to the column along with two additional 5 ml rinses. Elute the column with an additional 90 mL of hexane and retain the entire eluate. Concentrate this solution to a volume of about 1 ml.

7.2 Basic Alumina Column: Cut off a 10 mL disposable Pasteur glass pipette at the 4 mL graduation mark and pack the lower section with glass wool (precleaned) and 3 g of Woelm basic alumina (prepared as described in the Reagent section of this protocol). Transfer the concentrated extract from the combination silica column to the top of the column and elute the column sequentially with 15 mL of hexane, 10 mL of 8% methylene chloride-in-hexane and 15 mL of 50% methylene chloride-in-hexane, discarding the first two eluate fractions and retaining the third eluate fraction. Concentrate the latter fraction to about 0.5 mL using the nitrogen blowdown apparatus described earlier.

7.3 PX-21 Carbon/Celite 545 Column: Take a 9 inch disposable Pasteur pipette and cut off a 0.5 inch section from the constricted tip. Insert a filter paper disk at the top of the tube, 2.5 cm. from the constriction. Add a sufficient quantity of PX-21 Carbon/Celite 545 (Prepared as described in the reagent section of this protocol) to the tube to form a 2 cm. length of the Carbon-Celite. Insert a glass wool plug. Preelute the column in sequence with 2 mL of 50% benzene-in-ethyl acetate, 1 mL of 50% methylene chloride-in-cyclohexane and 2 mL of hexane, and discard these eluates. Load the extract (in 1 mL of hexane) from the alumina column onto the top of the column, along with 1 mL hexane rinse. Elute the column with 2 mL of 50% methylene chloride-in-hexane and 2 mL of 50% benzene-in-ethyl acetate and discard these eluates. Invert the column and reverse elute it with 4 mL of toluene, retaining this eluate. Concentrate the eluate and transfer it to a Reacti-Vial for storage. Store extracts in a freezer, shielded from light, prior

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to GC-MS analysis. If desired, still another column chromatographic clean-up step can be employed prior to concentration of the extract, as described below.

7.4 Silica/Diol Micro Column Cleanup: After the above clean-up steps small amounts of highly colored polar compounds may be present in complex samples. These are removed, if necessary, by the following column: Push a small plug of glass wool into a disposable 6 mm i.d. glass Pasteur pipette, followed by 3 mm of Sepralyte (Analytichem International), 6 mm of silica gel and finally 3 mm of sodium sulfate. The column is pre-wet with hexane, the sample is applied in 100 µL of 100% hexane and eluted with hexane, collecting 1.5 ml.

8. Procedure for Analysis of Sample Extracts for PCDD/PCDF Using Gas Chromatography-Mass Spectrometry (GC-MS).

8.1 Sample extracts prepared by the procedures described in the foregoing are analyzed by GC-MS utilizing the following instrumental parameters. Typically, 1 to 5 µL portions of the extract are injected into the GC. Sample extracts are first analyzed using the DB-5 capillary GC column to obtain data on the concentrations of total tetra-through octa-CDDs and CDFs, and on 2,3,7,8-TCDD. If tetra-CDFs are detected in this analysis, then another aliquot of the sample is analyzed in a separate run, using the DB-225 column to obtain data on the concentration of 2,3,7,8-TCDF.

8.2 Gas Chromatograph

8.2.1 Injector: Configured for capillary column, splitless/split injection (split flow on 60 seconds following injection), injector temperature, 250°C.

8.2.2 Carrier gas: Hydrogen, 30 lb head pressure.

8.2.3 Capillary Column 1: For total tetra- through octa - CDDs/CDFs and 2,3,7,8-TCDD, 60 M x 0.25 mm I.D. fused silica DB-5; temperature programmed (see Table 1 for temperature program). Capillary Column 2: for 2,3,7,8-TCDF only, 60 M x 0.25 mm I.D. fused silica DB-225, temperature programmed (180°C for 1 min., then increase from 180°C to 240°C @ 5°C/min., hold at 240°C for 1 min.)

8.2.4 Interface Temperature: 250°C

8.3 Mass Spectrometer

8.3.1 Ionization Mode: Electron impact (70 eV)

8.3.2 Static Resolution: 1:600 (10% valley) or 1:10,000 depending upon requirements. Usually the sample extracts are initially analyzed using low resolution MS, then if PCDD/PCDF are detected, it is desirable to analyze a second portion of the sample extract using high resolution MS.

8.3.3 Source Temperature: 250°C

8.3.4 Ions Monitored: Computer-Controlled Selected-Ion Monitoring. See Table 1 for list of ion masses monitored and time intervals during which ions characteristic of each class of CDDs and CDFs are monitored.

8.4 Calibration Procedures:

8.4.1 Calibrating the MS Mass Scale: Perfluoro Kerosene, decafluorotriphenyl phosphine, or any other accepted mass marker compound must be introduced into the MS, in order to calibrate the mass scale through at least m/z 500. The procedures specified by the manufacturer for the particular MS instrument used are to be employed for this purpose. The mass calibration should be rechecked at least at 8 hr. operating intervals.

8.4.2 Table 1 shows the GC temperature program typically used to resolve each chlorinated class of PCDD and PCDF from the other chlorinated classes, and indicates the corresponding time intervals during which ions indicative of each chlorinated class are monitored by the MS. This temperature program and ion monitoring time cycle must be established by each analyst for the particular instrumentation used by injecting aliquots of Standard Mixtures C, D, and E (See earlier section of this protocol for description of these mixtures). It may be necessary to adjust the temperature program and ion monitoring cycles slightly based on the observations from analysis of these mixtures.

8.4.3 Checking GC Column Resolution for 2,3,7,8-TCDD and 2,3,7,8-TCDF: Utilize the column-resolution TCDD and TCDF isomer mixtures (Standard Mixtures D and E, containing 50 pg/µl, respectively of the appropriate TCDD and TCDF isomers) to verify that 2,3,7,8-TCDD and 2,3,7,8-TCDF are separated from the other TCDD and TCDF isomers, respectively. A 20% valley or less must be obtained between the mass chromatographic peak observed for 2,3,7,8-TCDD and adjacent peaks arising from other TCDD isomers, and similar separation of 2,3,7,8-TCDF from other neighboring TCDFs, is required. Standard Mixture D is utilized with the DB5 column and Standard Mixture E with the DB-225 column. Analyze the column performance standards using the instrumental parameters specified in Sections 8.2 and 8.3, and in Table 1. The column performance evaluation must be performed each time a new column is installed in the gas chromatograph, and at least once during each 8 hour operating period. Providing that the same column is employed for a

period of time, its performance can also be gauged by noting the peak width (at 1/2 peak height) for 2,3,7,8-TCDD or for 2,3,7,8-TCDF. If this peak width is observed to broaden by 20% or more as compared to the usual width for satisfactory operation, then the column resolution is suspect and must be checked. If the column resolution is found to be insufficient to resolve 2,3,7,8-TCDD and 2,3,7,8-TCDF from their neighboring TCDD and TCDF isomers, respectively, (as measured on the two different columns used for resolving these two isomers), then a new DB-5 and/or DB-225 GC column must be installed.

8.4.4 Calibration of the GC-MS-DS system to accomplish quantitative analysis of 2,3,7,8-TCDD and 2,3,7,8-TCDF, and of the total tetra- through octa-CDDs and CDFs contained in the sample extract, is accomplished by analyzing a series of at least three working calibration standards. Each of these standards is prepared to contain the same concentration of each of the stable-isotopically labelled internal standards used here (Standard Mixture A) but a different concentration of native PCDD/PCDF (Standard Mixture C). Typically, mixtures will be prepared so that the ratio of native PCDD and PCDF to isotopically-labelled PCDD and PCDF will be on the order of 0.1, 0.5 and 1.0 in the three working calibration mixtures. The actual concentrations of both native and isotopically-labelled PCDD and PCDF in the working calibration standards will be selected by the analyst on the basis of the concentrations to be measured in the actual sample extracts. At the time when aliquots of each of the standards are injected (and also when injecting aliquots of actual sample extracts), if desired, an aliquot of a standard containing typically 1 ng of $^{37}Cl_4$-2,3,7,8-TCDD (Standard B) can be drawn into the micro syringe containing the calibration solution described above (or the sample extract) and this is then co-injected along with the sample extract in order to obtain data permitting calculation of the percent recovery of the $^{13}C_{12}$-2,3,7,8-TCDD internal standard. Equations for calculating relative response factors from the calibration data derived from the calibration standard analyses, and for calculating the recovery of the $^{13}C_{12}$-2,3,7,8-TCDD and the other isotopically-labelled PCDD and PCDF, and the concentration of native PCDD and PCDF in the sample (from the extract analysis), are summarized below. In these calculations, as can be seen, 2,3,7,8-TCDD is employed as the illustrative model. However, the calculations for each of the other native dioxins and furans in the sample analyzed are accomplished in an analgous manner. It should be noted that in view of the fact that stable-isotopically labelled internal standards corresponding to each tetra- through octachlorinated class are not used here (owing to limited availability at this time) the following approach is adopted: For quantitation of tetrachlorinated dibenzofurans $^{13}C_{12}$-2,3,7,8-TCDF is used as the internal standard. For quantitation of tetrachlorodibenzo-p-dioxins, $^{13}C_{12}$-2,3,7,8-TCDD is used as the internal standard. For quantitation of PeCDD, HxCDD, PeCDF, and HxCDF, the corresponding stable-isotopically labelled HxCDD and HxCDF internal standards are used. For quantitation of HpCDD, OCDD, and HpCDF, OCDF, the isotopically-labelled OCDD and OCDF, respectively, are used. Inherent in this approach is the assumption that the response factors for each of the isomers

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f each chlorinated class are the same, and in the case of the penta- d hepta-CDDs and CDFs, the assumption is made that the responses for ese two classes are equivalent to those for the tetra-isomers and the cta-isomers, respectively.

8.4.5 Equations for Calculating Response Factors, Concentration of ,3,7,8-TCDD in An Unknown Sample, and Recoveries of Internal Standards.

quation 1: Response Factor (RRF) for native 2,3,7,8-TCDD using $^{13}C_{12}$-2,3,7,8-TCDD as an internal standard.

RRF_d = $(A_s C_{is}/A_{is} C_s)$

where: A_s = SIM response for 2,3,7,8-TCDD ion at m/z 320 + 322

A_{is} = SIM response for $^{13}C_{12}$-2,3,7,8-TCDD internal standard ion at m/z 332

C_{is} = Concentration of the internal standard (pg./µL.)

C_s = Concentration of the 2,3,7,8-TCDD (pg./µL.)

Equation 2: Response Factor (RRF) for $^{37}Cl_4$-2,3,7,8-TCDD, the co-injected external standard

RRF_f = $(A_{is} C_{es})/(A_{es} C_{is})$

where: A_{is} = SIM response for $^{13}C_{12}$-2,3,7,8-TCDD internal standard ion at m/z 332

A_{es} = SIM response for co-injected $^{37}Cl_4$-2,3,7,8-TCDD external standard at m/z 328 - 0.009 (SIM response for native 2,3,7,8-TCDD at m/z 322)

C_{is} = Concentration of the internal standard (pg./µL.)

C_{es} = Concentration of the external standard (pg./µL.)

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Equation 3: Calculation of concentration of native 2,3,7,8-TCDD using $^{13}C_{12}$-2,3,7,8-TCDD as internal standard

Concentration, pg./g. = $(A_s)(I_s)/(A_{is})(RRF_d)(W)$

where: A_s = SIM response for 2,3,7,8-TCDD ion at m/z 320 + 322

A_{is} = SIM response for the $^{13}C_{12}$-2,3,7,8-TCDD internal standard ion at m/z 332

I_s = Amount of internal standard added to each sample (pg.)

W = Weight of soil or waste in grams

RRF_d = Relative response factor from Equation 1

Equation 4: Calculation of % recovery of $^{13}C_{12}$-2,3,7,8-TCDD internal standard

% Recovery = $100(A_{is})(E_s)/(A_{es})(I_i)(RRF_f)$

A_{is} = SIM response for $^{13}C_{12}$-2,3,7,8-TCDD internal standard ion at m/z 332

A_{es} = SIM response for $^{37}Cl_4$-2,3,7,8-TCDD external standard ion at m/z 328 - 0.009 (SIM Response for native 2,3,7,8-TCDD at m/z 322)

E_s = Amount of $^{37}Cl_4$-2,3,7,8-TCDD external standard co-injected with sample extract (ng.)

I_i = Theoretical amount of $^{13}C_{12}$-2,3,7,8-TCDD internal standard in injection

RRF_f = Relative response factor from Equation 2

As noted above, procedures similar to these are applied to calculate analytical results for all of the other PCDD/PCDF determined in this method.

8.5 Criteria Which GC-MS Data Must Satisfy for Identification of PCDD/PCDF in Samples Analyzed and Additional Details of Calculation Procedures.

In order to identify specific PCDD/PCDF in samples analyzed, the GC-MS data obtained must satisfy the following criteria:

8.5.1 Mass spectral responses must be observed at both the molecular and fragment ion masses corresponding to the ions indicative of each chlorinated class of PCDD/PCDF identified (see Table 1) and intensities of these ions must maximize essentially simultaneously (within ± 1 second). In addition, the chromatographic retention times observed for each PCDD/PCDF signal must be correct relative to the appropriate stable-isotopically labelled internal standard and must be consistent with the retention time windows established for the chlorinated group to which the particular PCDD/PCDF is assigned.

8.5.2 The ratio of the intensity of the molecular ion $(M)^+$ signal to that of the $(M+2)^+$ signal must be within ± 10% of the theoretically expected ratio (for example, 0.77 in the case of TCDD; therefore the acceptable range for this ratio is 0.69 to 0.85).

8.5.3 The intensities of the ion signals are considered to be detectable if each exceeds the baseline noise by a factor of at least 3:1. The ion intensities are considered to be quantitatively measurable if each ion intensity exceeds the baseline noise by a factor of at least 5:1[c].

8.5.4 For reliable detection and quantitation of PCDF it is also desirable to monitor signals arising from chlorinated diphenyl ethers which, if present could give rise to fragment ions yielding ion masses identical to those monitored as indicators of the PCDF. Accordingly, in Table 1, appropriate chlorinated diphenyl ether masses are specified which must be monitored simultaneously with the PCDF ion-masses. Only when the response for the diphenyl ether ion mass is not detected at the same time as the PCDF ion mass can the signal obtained for an apparent PCDF be considered unique.

8.5.5 Measurement of the concentration of the congeners in a chlorinated class using the methods described herein is based on the assumption that all of the congeners are identical to the calibration standards employed in terms of their respective chemical and separation properties and in terms of their respective gas chromatographic and mass spectrometric responses. Using these assumptions, for example, the $^{13}C_{12}$-2,3,7,8-TCDD internal standard is utilized as the internal calibration standard for all of the 22 TCDD isomers or congeners. Furthermore, the concentration of the total TCDD present in a sample extract is determined by calculating, on the basis of the standard procedure outlined above, the concentration of each TCDD isomer peak (or peaks for multiple TCDD isomers, where these coelute) and these individual concentrations are subsequently summed to obtain the concentration of "total" TCDD.

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[c] In practice, the analyst can estimate the baseline noise by measuring the extension of the baseline immediately prior to each of the two mass chromatographic peaks attributed to a given PCDD or PCDF. Spurious signals may arise either from electronic noise or from other organic compounds in the extract. Since it may be desirable to evaluate the judgement of the analyst in this respect, copies of original mass chromatograms must be included in the report of analytical results.

8.6 Frequently, during the analysis of actual sample extracts, extraneous compounds which are present in the extract (those organic compounds not completely removed during the clean-up phase of the analysis) can cause changes in the liquid and gas chromatographic elution characteristics of the PCDD/PCDF (typically retention times for the PCDD/PCDF are prolonged). Such extraneous organic compounds, when introduced into the mass spectrometer source may also result in a decrease in the sensitivity of the MS because of suppression of ionization, and other affects such as charge transfer phenomena. The shifts in chromatographic retention times are usually general shifts, that is, the relative retention times for the PCDD/PCDF are not changed, although the entire elution time scale is prolonged. The analyst's intervention in the GC-MS operating sequence can correct for the lengthened GC retention times which are sometimes observed due to the presence of extraneous organics in the sample extract. For example, using the program outlined in Table 1, if the retention time observed for 2,3,7,8-TCDD (which normally is 19.5 minutes) is lengthened by 30 seconds or more, appropriate adjustments in the programming sequence outlined in Table 1 can be made, that is, each selected ion-monitoring program is delayed by a length of time proportionate to the lengthening of the retention time for the 2,3,7,8-TCDD isomer. In the case of ionization suppression, this phenomenon is inherently counteracted by the internal standard approach. However, if loss of sensitivity due to ionization suppression is severe, additional clean-up of the sample extract may be required in order to achieve the desired detection limits.

9. Quality Assurance/Quality Control

9.1 Quality assurance and quality control are ensured by the following provisions:

9.1.1 Each sample analyzed is spiked with stable isotopically labelled internal standards, prior to extraction and analysis. Recoveries obtained for each of these standards should typically be in the range from 60-90%. Since these compounds are used as true internal standards however, lower recoveries do not necessarily invalidate the analytical results for native PCDD/PCDF, but may result in higher detection limits than are desired.

9.1.2 Processing and analysis of at least one method blank sample is accomplished for each set of samples (a set being defined as 20 samples or less).

9.1.3 It is desirable to analyze at least one sample spiked with representative native PCDD/PCDF for each set of 20 or fewer samples. The result of this analysis provides an indication of the efficacy of the entire analytical procedure. The results of this analysis will be considered acceptable if the detected concentration of each of the native

CDD/PCDF added to the sample is within ±50% of the known concentration. An appropriate set of native isomers to be added here is a set such s that indicated for Standard Mixture C.)

9.1.4 At least one of the samples analyzed out of each set (of 20 amples or less) is analyzed in duplicate and the results of the duplicate nalysis are included in the report of data.

9.1.5 Performance evaluation samples prepared by EPA,or other aboratories,which contain representative PCDD/PCDF in concentrations pproximating those present in typical field samples being analyzed but unknown to the analyzing lab) should be periodically distributed o laboratories accomplishing these analyses.

9.1.6 Sources of all calibration and performance standards used in the nalyses and the purity of these materials must be specified in the data eport.

). Data Reporting

10.1 Each report of analyses accomplished using the protocol lescribed herein will typically include tables of results which include the following:

10.1.1 Complete identification of the samples analyzed (sample numbers and source).

10.1.2 The dates and times at which all analyses were accomplished. This information should also appear on each mass chromatogram included with the report.

10.1.3 Raw mass chromatographic data which consists of the absolute intensities (based on either peak height or peak area) of the signals observed for the ion-masses monitored (See Table 1).

10.1.4 The calculated ratios of the intensities of the molecular ions for all PCDD/PCDF detected.

10.1.5 The calculated concentrations of native 2,3,7,8-TCDD and 2,3,7,8-TCDF, and the total concentrations of the congeners of each class of PCDD/PCDF for each sample analyzed, expressed in nanograms TCDD per gram of sample (that is, parts-per-billion) as determined from the raw data. If no PCDD/PCDF are detected, the notation "Not Detected" or "N.D." is used, and the minimum detectable concentrations (or detection limits) are reported.

10.1.6 The same raw and calculated data which are provided for the actual samples will also be reported for the duplicate analyses, the method blank analyses, the spiked sample analyses and any other QA or performance samples analyzed in conjunction with the actual sample set(s).

10.1.7 The recoveries of the internal standards in percent.

10.1.8 The recoveries of the native PCDD/PCDF from spiked samples in percent.

10.1.9 The calibration data, including response factors calculated from the three point calibration procedure described elsewhere in this protocol. Data showing that these factors have been verified at least once during each 8 hour period of operation or with each separate set of samples analyzed must be included.

10.1.10 The weight or quantity of the original sample analyzed.

10.1.11 Documentation of the source of all PCDD/PCDF standards used and available specifications on purity.

10.1.12 In addition to the tables described above, each report of analyses will include all mass chromatograms obtained for all samples analyzed, as well as for all calibration, GC column performance, and GC "window" definition runs and results of column performance checks.

10.1.13 Any deviations from the procedures described in this protocal which are applied in the analyses of samples will be documented in detail in the analytical report.

11. Typical Data Indicative of Method Performance - Precision and Accuracy.

11.1 The method described herein has typically been employed to quantitatively determine 2,3,7,8-TCDD in combustion product samples at concentrations as low as 10 picograms/gram and as high at 100 μg/g. Concentrations of the other PCDD/PCDF which can be detected typically fall within the range of 20 picograms/isomer/gram of sample, to 100 picograms/g of sample. Of course, the limits of detection which can be practically achieved are dependent on the quantity of sample available

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..d th. unt :ind ther rfer orga esi whicl present in the sample. With respect to precision, the average deviation of data obtained from the analyses of a number of aliquots of the same sample containing the 2,3,7,8-TCDD isomer in the 250-300 ppb range is estimated to be +10% or better. Data on the precision of quantitation of multiple PCDD/PCDF in a single sample are not as yet available. As yet, there is inadequate interlaboratory and performance evaluation data available to specify the accuracy which can be expected of the analytical procedures described herein.

TABLE 1. Sequence of Operations in GC-MS-DS Quantitation of PCDDs/PCDFs in Extracts of Environmental Samples

Elapsed Time (min)	Event	GC Column Temperature* (°C)	Temperature Program Rate (°C/min)	Ions Monitored by Mass Spectrometer (m/z)	Identity of Fragment Ion	Compounds Monitored	Approximate Theoretical Ratio of [M]	M+2
0.00	Injection, splitless	190						
1.00	Turn on split valve	190						
1.00	Begin temp. program to 220°C	190	5					
6.00	Open column flow to mass spectrometer	215	5					
7.00	Column temperature hold	220						
14.00	Start Tetra Program; sweep = 350 ppm; time/mass = 0.08 sec.			240.938	$[M-COCl]^+$	TCDF		
				258.930	$[M-COCl]^+$	TCDD		
				303.902	$[M]^+$	TCDF	0.77	
				305.899	$[M+2]^+$	TCDF		
				315.942	$[M]^+$	$^{13}C_{12}$-TCDF		
				319.897	$[M]^+$	TCDD	0.	
				321.894	$[M+2]^+$	TCDD		
				327.885	$[M]^+$	$^{37}Cl_4$-TCDD		
				331.937	$[M]^+$	$^{13}C_{12}$-TCDD		
				373.840	$[M]^+$	HxDPE^{a}.		
22.00	Stop Tetra Program	220						
22.80	Start Penta Program; sweep = 350 ppm; time/mass = 0.12 sec.			274.899	$[M-COCl]^+$	PeCDF		
				290.894	$[M-COCl]^+$	PeCDD		
				337.863	$[M]^+$	PeCDF	0.61	
23.00	Begin temp. program to 235°	220	5	339.860	$[M+2]^+$	PeCDF		
26.00	Column temperature hold	235		353.858	$[M]^+$	PeCDD	0.	
				355.855	$[M+2]^+$	PeCDD		
				407.801	$[M]^+$	HpDPE^{a}.		
32.00	Stop Penta Program							
32.50	Start Hexa Program; sweep = 350 ppm; time/mass = 0.20 sec.	235		310.857	$[M-COCl]^+$	HxCDF		
				326.852	$[M-COCl]^+$	HxCDD		
				373.821	$[M]^+$	HxCDF	1.	
				375.821	$[M+2]^+$	HxCDF		
				385.861	$[M]^+$	$^{13}C_{12}$-HxCDF		
				389.816	$[M]^+$	HxCDD	1.23	
				391.813	$[M+2]^+$	HxCDD		
				411.856	$[M]^+$	$^{13}C_{12}$-HxCDD		
				443.759	$[M]^+$	OCDPE^{a}.		

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TABLE 1. Sequence of Operations in GC-MS-DS Quantitation of PCDDs/PCDFs in Extracts of Environmental Samples (Cont.)

lapsed ime min)	Event	GC Column Temperature (°C)	Temperature Program Rate (°C/min)	Ions Monitored by Mass Spectrometer (m/z)	Identity of Fragment Ion	Compounds Monitored	Approximate Theoretical Ratio of [M]+:[M+2]+
3.00	Begin temp. program to 250°C	235	5				
6.00	Column temperature hold	250					
2.50	Stop Hexa Program						
3.00	Start Hepta Program; sweep =	250		344.818	[M-COCl]+	HpCDF	
	350 ppm; time/mass = 0.30 sec.			360.813	[M-COCl]+	HpCDD	
				407.782	[M]+	HpCDF	1.03
				409.779	[M+2]+	HpCDF	
				423.777	[M]+	HpCDD	1.03
				425.774	[M+2]+	HpCDD	
				477.720	[M+]	NDPE^a.	
3.00	Stop Hepta Program	250					
3.50	Start Octa Program; sweep =	250		378.768	[M-COCl]+	OCDF	
	350 ppm; time/mass = 0.30 sec.			394.774	[M-COCl]+	OCDD	
				441.732	[M]+	OCDF	0.88
54.00	Begin temp. program to 270°	250°	5	443.740	[M+2]+	OCDF	
58.00	Column temperature hold	270°		453.772	[M]+	$^{13}C_{12}$-OCDF	
				457.738	[M]+	OCDD	0.88
				459.735	[M+2]+	OCDD	
				469.779	[M]+	$^{13}C_{12}$-OCDD	
				471.776	[M+2]+	$^{13}C_{12}$-OCDD	
				511.681	[M]+	DDPE^a.	
65.00	Stop Octa Program						
65.00	Begin temp. program to 300°	270°	5				
71.00	Column temperature hold	300°					
75.00	Cool Column to 190°						

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[a] HxDPE, HpDPE, ODPE, NDPE, DDPE are abbreviations which designate (respectively) hexachloro-, heptachloro-, octachloro-, nonachloro-, and decachlorodiphenyl ethers.

*The parameters given here are applicable for a 60-meter fused silica capillary GC column coated with DB-5.

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APPENDIX

RECOMMENDED SAFETY AND HANDLING PROCEDURES

FOR LABORATORIES CONDUCTING PCDD/PCDF ANALYSES

ecommended Safety and Handling Procedures in Connection with Implementing he Analytical Protocal for Determination of PCDD/PCDF in Combustion Products

1. The human toxicology of PCDD/PCDF is not well defined at present, lthough the 2,3,7,8-TCDD isomer has been found to be acnegenic, arcinogenic, and teratogenic in the course of laboratory animal tudies. The 2,3,7,8-TCDD is a solid at room temperature, and has a elatively low vapor pressure. The solubility of this compound in ater is only about 200 parts-per-trillion, but the solubility in arious organic solvents ranges from about 0.001% to 0.14%. The physical roperties of the 135 other tetra-through octachlorinaed PCDD/PCDF have not een well established, although it is presumed that the physical roperties of these congeners are generally similar to those of the ,3,7,8-TCDD isomer. On the basis of the available toxicological nd physical property data for TCDD, this compound, as well as the other CDD and PCDF, should be handled only by highly trained personnel ho are thoroughly versed in the appropriate procedures, and who nderstand the associated risks.

2. PCDD/PCDF and samples containing these are handled using essentially the same techniques as those employed in handling radioactive or infectious materials. Well-ventilated, controlled-access laboratories re required, and laboratory personnel entering these laboratories should ear appropriate safety clothing, including disposable coveralls, shoe covers, gloves, and face and head masks. During analytical operations which may give rise to aerosols or dusts, personnel should wear respirators equipped with activated carbon filters. Eye protection equipment (preferably full face shields) must be worn at all times while working in the analytical laboratory with PCDD/PCDF. Various types of gloves can be used by personnel, depending upon the analytical operation being accomplished. Latex gloves are generally utilized, and when handling samples thought to be particularly hazardous, an additional set of gloves is also worn beneath the latex gloves (for example, Playtex gloves supplied by American Scientific Products, Cat. No. 67216). Bench-tops and other work surfaces in the laboratory should be covered with plastic-backed absorbent paper during all analytical processing. When finely divided samples (dusts, soils, dry chemicals) are being processed, removal of these from sample containers, as well as other operations, including weighing, transferring, and mixing with solvents, should all be accomplished within a glove box. Glove boxes, hoods and the effluents from mechanical vacuum pumps and gas chromatographs on the mass spectrometers should be vented to the atmosphere preferably only after passing through HEPA particulate filters and vapor-sorbing charcoal.

3. All laboratory ware, safety clothing and other items potentially contaminated with PCDD/PCDF in the course of analyses must be carefully secured and subjected to proper disposal. When feasible, liquid wastes

are concentrated, and the residues are placed in approved steel hazardous waste drums fitted with heavy gauge polyethylene liners. Glass and combustible items are compacted using a dedicated trash compactor used only for hazardous waste materials and then placed in the same type of disposal drum. Disposal of accumulated wastes is periodically accomplished by high temperature incineration at EPA-approved facilities.

4. Surfaces of laboratory benches, apparatus and other appropriate areas should be periodically subjected to surface wipe tests using solvent-wetted filter paper which is then analyzed to check for PCDD/PCDF contamination in the laboratory. Typically, if the detectable level of TCDD or TCDF from such a test is greater than $50ng/m^2$, this indicates the need for decontamination of the laboratory. A typical action limit in terms of surface contamination of the other PCDD/PCDF (summed) is $500ng/m^2$. In the event of a spill within the laboratory, absorbent paper is used to wipe up the spilled material and this is then placed into a hazardous waste drum. The contaminated surface is subsequently cleaned thoroughly by washing with appropriate solvents (methylene chloride followed by methanol) and laboratory detergents. This is repeated until wipe tests indicate that the levels of surface contamination are below the limits cited.

5. In the unlikely event that analytical personnel experience skin contact with PCDD/PCDF or samples containing these, the contaminated skin area should immediately be thoroughly scrubbed using mild soap and water. Personnel involved in any such accident should subsequently be taken to the nearest medical facility, preferably a facility whose staff is knowledgable in the toxicology of chlorinated hydrocarbons. Again, disposal of contaminated clothing is accomplished by placing it in hazardous waste drums.

6. It is desirable that personnel working in laboratories where PCDD/PCDF are handled be given periodic physical examinations (at least yearly). Such examinations should include specialized tests, such as those for urinary porphyrins and for certain blood parameters which, based upon published clinical observations, are appropriate for persons who may be exposed to PCDD/PCDF. Periodic facial photographs to document the onset of dermatologic problems are also advisable.